

# Novel Solid Contact Ion Selective Sensor for Potentiometric Analysis of Barium Ions

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**Abstract**: Barium as an alkaline earth metal is widely used in multiple industries. Due to its widespread use, it is toxic to living things in high concentrations. In this study, polymer membrane barium-selective potentiometric sensors were prepared in which 4-aminobenzoic acid 2-diethylaminoethyl ester was used as an ionophore. The prepared sensors exhibited selective and stable behavior towards barium ions. The novel barium-selective potentiometric sensor had a low detection limit of  $4.23 \times 10^{-6}$  M over a wide linear concentration range from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  M. The sensor proposed in the present study had good repeatability, short response time (8s) and could work over a wide range of pH. The sensors prepared simply and economically were able to determine barium ions in various samples with very high recoveries.

**Keywords:** Barium, sensor, potentiometry, ion-selective electrodes.

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# 1. INTRODUCTION

Barium occurs naturally in the food and groundwater, and its water-soluble salts are toxic (Kravchenko et al., 2014; Gad, 2014). Barium is commonly used in various industrial sectors such as the petroleum industry, electroplating, alloying, glass industry, and also in pigments and corrosion protection films (Grajeda et al., 2017; Modi et al., 2014). Due to its widespread use in industry, barium pollutes both soil and water. High concentrations of barium can be toxic to living things (Oliveira et al., 2012; Llugany et al., 2000). Especially in humans, it can cause a number of health problems such as respiratory failure, hypophosphatemia, loss of reflexes and rhabdomyolysis (Altunoluk et al., 2024). To date, inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS) and spectroscopic methods have been proposed for the determination of barium in various samples (Ardianrama et al., 2020; Bisergaeva et al., 2020; Huelga-Suarez et al., 2013). These methods, which are not particularly suitable for on-site analysis, are complicated to use, time-consuming, costly, and require experienced personnel and a well-equipped laboratory (Özbek, 2023; Abu Shawish et al., 2020).

Potentiometric methodologies, which have a highly important place in electrochemistry, are a subject intensively studied by sensor researchers (Berkel and Özbek, 2024). Potentiometry is an electrochemical method in which the potential of an electrode system consisting of reference and working electrodes is measured against time (Isildak and Özbek, 2021). Potentiometric ion-selective electrodes (ISEs) have important advantages such as easy use, short response time, low limit of detection, wide range of concentration, low cost, low-energy consumption, good selectivity and repeatability (Abu Shawish et al., 2016; Özbek et al., 2024a; Wu et al., 2023; Verma et al., 2023). ISEs are applied in many fields, for instance in the analysis of food, pharmaceutical, agriculture, medicine and environmental samples (Özbek and Isildak, 2022; Özbek and Altunoluk 2024). ISEs can be prepared using a wide variety of materials (Özbek et al., 2022a).

Ionophores are molecules that are both commercially available and synthesized. These molecules are the most important sensor material that can selectively interact with the analyte (Özbek et al., 2022a; Ören et al., 2024). Ionophores are undoubtedly the most critical components that influence the electrode's selectivity towards a single ion as well as other commonly used ions. 3-deoxy-D-erythro-hexos-2-

ulose bis(thiosemicarbazone) (Zamani et al., 2010), 2,3,4-pyridine-1,3,5,7,12-pentaazacyclopentadeca-3-ene (Singh et al., 2005), 4-4'-methylenediantipyrine (Abedi et al., 2008), and organophosphorus compounds (Saleh, 2000) have been previously used as ionophores in the selective determination of barium ions as reported in the literature. In the current study, we developed new ion-selective sensors that exhibit high selectivity to barium ions by using the 4-aminobenzoic acid 2diethylaminoethyl ester (Figure 1) molecule as an ionophore. 4-aminobenzoic acid 2-diethylaminoethyl is also a local anesthetic drug (Özbek and Altunoluk, 2024). This study aimed to investigate the ionophore properties of its chemical form.



Figure 1. Chemical structure of the ionophore.

## 2. EXPERIMENTAL SECTION

#### 2.1. Chemicals and Apparatus

Graphite, high molecular weight poly(vinyl chloride) (PVC), 4-aminobenzoic acid 2-diethylaminoethyl ester (ionophore;  $\geq$ 97%), plasticizers, anion excluder, tetrahydrofuran (THF;  $\geq$ 99.9%), sodium hydroxide (NaOH;  $\geq$ 98.0%), nitric acid (HNO<sub>3</sub>) and metal nitrate salts were of the greatest analytical purity and were obtained from Sigma-Aldrich. All potential measurements were made with an Ag/AgCl reference electrode (Thermo Scientific) connected to a multi-channel potentiometer (Medisen Medical Ltd. Sti., Turkey) and the prepared sensors.

#### 2.2. Method

In this study, the preparation of solid contact PVC membrane barium-selective sensors were performed in two stages, as in our previous studies (Özbek et al., 2024b; Özbek et al., 2022b). Initially, conductive solid contact mixtures were prepared by dissolving 50.0 mg graphite, 35.0 mg epoxy and 15.0 mg hardener in approximately 3 mL THF. Copper wires then were dipped into the homogeneous solid contact mixture 3–4 times and subsequently left to dry in the dark for 24 h. Then, polymer membrane mixtures were prepared by dissolving them in the solution of THF with the compositions in Table 1. Mixtures containing ionophore, PVC, plasticizer and anion excluder were dissolved in approximately 3 mL of THF. After a homogeneous mixture was provided, the mixtures reaching a certain viscosity were coated on the surface of previously prepared solid contact electrodes. The surface of pre-prepared conductive solid contact electrodes were covered with these mixtures and allowed to dry. Potentiometric measurements were conducted using barium ion solutions with the prepared sensors. The preparation steps and potentiometric measurement system of the new barium-selective sensors were summarized in Figure 2.



Figure 2. Preparation stages of barium-selective sensors.

# 3. RESULTS AND DISCUSSION

In the current study, sensors with a total of seven different compositions were designed using 3 different plasticizers (namely, dibutyl phthalate (DBP), bis(2–ethylhexyl)sebacate (BEHS) and *o*–

nitrophenyloctyl ether (*o*–NPOE)). Plasticizers reduce the viscosity of the polymer matrix and provide mobility of the components in the membrane structure. In the literature, the most commonly used composition of PVC membrane electrodes was reported as 1-7% ionophore, 28-33% PVC, 60-69%

plasticizer and 0.03-10% anion excluder (Erol et al., 2009). The potentiometric performance characteristics of the sensors prepared in these ranges were investigated using Ba<sup>2+</sup> ion solutions. Barium ion solutions were prepared with Ba(NO<sub>3</sub>)<sub>2</sub>. The potentiometric performance features of the prepared sensors were given in Table 1. According to the obtained data, mixture number VII among the

prepared sensors had the lowest detection limit  $(4.23 \times 10^{-6} \text{ M})$  in a wide concentration range of  $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$  M. When the potentiometric performance properties of the prepared sensors were evaluated, the most ideal composition was determined to be 3.0% ionophore, 32.0% PVC, 64.0% BEHS and 1.0% KTpCIPB.

Table 1. Certain	performance f	eatures of the	prepared barium	-selective	potentiometric	sensors
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Sensor composition $(w/w)$				Poter	ntiometric per	formance				
No	PVC	Ionophore	BEHS	Plasticize C	o-NPOE	KT <i>p</i> CIPB	Linear Range, M	Detection Limit, M	Slope (mV/ decade)	R <sup>2</sup>
1	32.0	3.0		64.0		1.0	1.0×10 <sup>-5</sup> -1.0×10 <sup>-3</sup>	1.08×10 <sup>-5</sup>	15.5 (±2.2)	0.9859
2	32.0	3.0			64.0	1.0	1.0×10 <sup>-5</sup> -1.0×10 <sup>-3</sup>	9.22×10 <sup>-6</sup>	10.1 (±1.5)	0.9860
3	32.0	4.0		63.0		1.0	1.0×10 <sup>-5</sup> -1.0×10 <sup>-1</sup>	9.97×10 <sup>-6</sup>	11.0 (±1.1)	0.9866
4	32.0	5.0		62.0		1.0	1.0×10 <sup>-4</sup> -1.0×10 <sup>-1</sup>	1.0×10 <sup>-4</sup>	21.0 (±1.2)	0.9779
5	32.0	4.0			63.0	1.0	1.0×10 <sup>-4</sup> -1.0×10 <sup>-1</sup>	9.77×10 <sup>-5</sup>	16.5 (±2.5)	0.9518
6	32.0	5.0			62.0	1.0	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	2.15×10 <sup>-5</sup>	24.0 (±3.4)	0.9825
7	32.0	3.0	64.0	)		1.0	1.0×10 <sup>-5</sup> -1.0×10 <sup>-1</sup>	4.23×10 <sup>-6</sup>	19.0 (±0.2)	0.9995

In this study, the behavior of sensors with and without ionophores in their composition against barium ions was tested in order to determine the influence of the ionophore used on the behavior of the sensor. For this purpose, the behavior of solid contact, without any ionophore (BEHS + PVC + KTpCIPB) and optimum (Sensor VII) electrodes

against barium ion solutions is presented in Figure 3. Based on this data, electrodes without ionophores in their composition did not give a linear response to barium ions. Consequently, it can be stated that the ionophore in the proposed sensor composition is able to interact with barium ions.



Figure 3. Response of electrodes with and without ionophore to barium ions.

The potential (mV)-time (s) behavior of this novel barium-selective sensor was presented in Figure 4a, which shows that the sensor displays a linear response in the concentration range from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  M. The detection limit of detection (LOD) the prepared sensor was calculated using the calibration curve in Figure 4b. The detection limit of the sensor

was calculated considering the recommendations reported by IUPAC (Buck et al., 1994). The potential value corresponding to the point where the horizontal and vertical axes intersect in Figure 3b was written in its place in the linear equation. The detection limit of the proposed sensor was calculated as  $4.23 \times 10^{-6}$  M. The repeatability performance of the prepared novel barium-selective potentiometric sensor was tested with barium ion solutions in three different concentrations (namely,  $10^{-1}$ ,  $10^{-2}$  and  $10^{-3}$  M). Figure 4c shows that the sensor demonstrates repeatable and stable performance for three different concentration values. The results given in Figure 4 (a–c) also indicates that the proposed sensor has a near–Nernstian response in addition to a low detection limit over a wide concentration range. Additionally, the sensor has a repeatable and stable behavior.



**Figure 4. a-)** The potentiometric response (E (mV)-time (s)), **b-)** calibration curve **c-)** repeatability of barium-selective sensor.

The response time of the newly developed bariumselective potentiometric sensor was investigated according to the guidelines recommended by IUPAC (Buck et al., 1994). For this purpose, the equilibrium time of the sensor from one concentration to another was determined. The sensor developed according to Figure 5 reaches equilibrium in approximately 8 seconds for a 10-fold concentration change and has a very fast response time.



Figure 5. The dynamic response time of the sensor developed in the present study.

One of the most essential characterization parameters of ion-selective electrodes is considered

to be their selectivity. Selectivity is the behavior of a sensor towards a single species in the presence of

diverse ionic species. In this study, ten different cationic species were used to test the selectivity of the prepared sensor against barium ions. Figure 6 indicates the response of the barium-selective potentiometric sensor to barium ions relative to other ions. Based on this data, the prepared sensor exhibited the highest potential values against barium ions. Selectivity coefficients  $(K_{A,B}^{pot})$  were calculated to mathematically express the selectivity of the ions used in the investigation of selectivity. Selectivity coefficients for different ions were calculated based on the separate solution method (SSM) defined by IUPAC (Umezawa et al., 2000). For this purpose, using the data obtained from potentiometric measurements, the potential value of every ion at the concentration of  $1.0 \times 10^{-2}$  M was written into the equation recommended by IUPAC, and the selectivity coefficients were then calculated for the ions in Table 2.

$$log K_{A,B}^{pot} = \frac{(E_{B} - E_{A})Z_{A}F}{RTln10} + (1 - \frac{Z_{A}}{Z_{B}})log a_{A}$$

where,  $K_{A,B}^{pot}$  = selectivity coefficient,  $a_A$  = activity of Ba(II),  $a_B$  = activity of interfering ion,  $z_A$  = charge of Ba(II),  $z_B$  = charge of interfering ion; R, T, and F have the usual meanings.

According to the data presented in the Table 2, the selectivity order of the examined cations varies as K<sup>+</sup> > Sr<sup>2+</sup> > Co<sup>2+</sup> > Mn<sup>2+</sup> > Ni<sup>2+</sup> > Na<sup>+</sup> > Zn<sup>2+</sup> > Mg<sup>2+</sup> > Li<sup>+</sup> > Cd<sup>2+</sup>. The developed sensor is around 100 fold more selective towards barium ions than the closest interfering type. Based on the data given in Figure 6 and Table 2, we can state that the proposed novel sensor is highly selective towards barium ions than other species.



Figure 6. Selectivity of the newly developed barium-selective sensor towards other ions.

Table 2. The selectivity of	coefficient of	f barium–se	elective	sensor.
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Interfering ions	$logK_{Ba(II),M^{+n}}$	$K_{Ba(II),M^{+n}}$
K+	-2.02	9.55×10 <sup>-2</sup>
Sr <sup>2+</sup>	-2.70	1.99×10 <sup>-3</sup>
Co <sup>2+</sup>	-3.28	5.25×10 <sup>-4</sup>
Mn <sup>2+</sup>	-3.65	2.24×10 <sup>-4</sup>
Ni <sup>2+</sup>	-3.82	1.51×10 <sup>-4</sup>
Na <sup>+</sup>	-3.79	1.62×10 <sup>-4</sup>
Zn <sup>2+</sup>	-3.89	1.29×10 <sup>-4</sup>
Mg <sup>2+</sup>	-4.16	1.92×10 <sup>-5</sup>
Li+	-4.36	4.36×10 <sup>-5</sup>
Cd <sup>2+</sup>	-4.53	2.95×10 <sup>-5</sup>

The working range of the prepared sensor in terms of pH was determined using nitric acid (for pH 2.0-7.0) and sodium hydroxide (for pH 8.0-12.0). The pH working range was studied for two different

concentration values,  $1.0 \times 10^{-2}$  and  $1.0 \times 10^{-3}$  M barium ion solution was added to the pH solutions previously prepared. Potentiometric measurements were taken with the prepared sensor. Potential-pH

graph was drawn with the obtained data. The pH working range of the barium-selective sensor is given in Figure 7 which points that pH remained constant between 5.0 and 11.0 at both concentration values. While the high potential values at pH values of less than 5.0 in  $1.0 \times 10^{-2}$  M concentration are due to the presence of hydronium ions, the low potential values at high pHs in both concentrations may be due

to the formation of Ba(OH)<sub>2</sub>. The low potential values at pH < 5.0 in  $1.0 \times 10^{-3}$  M concentration may suggest that the sensor exhibits an unstable behavior in this acidic environment. Combined, it can be suggested that the newly proposed sensor can work stably at different concentration values independently of pH changes.



Figure 7. pH working range of the newly proposed barium-selective sensor.

Analytical applications of the produced sensors are an important indicator of sensor performance. In particular, applications in different matrices are necessary to demonstrate the selectivity and reliability of the sensor against a single ion. Therefore, applications of ISEs in real samples are of great importance. Analytical applications of the prepared novel barium-selective potentiometric sensor were conducted using different water and tea samples. Barium ions were added to these samples in the amounts presented in Table 3, and subsequently potential values were measured with the newly developed sensor. The amount of barium added in the real samples was calculated by substitution of the potential values into the linear equation. Consequently, it was observed that the developed sensor can detect barium ions with high recoveries (>90.0%). The obtained results show that the sensor can give reliable results in the determination of barium ions in different matrices.

Real Samples		Ba <sup>2+</sup> quantity, (M)	
	Added Ba <sup>2+</sup>	Found (± SD) with sensor*	% Recovery
Bottled water		9.57 (±0.35) ×10 <sup>-4</sup>	95.7
Теа	1.0×10 <sup>-3</sup>	9.55 (±0.25) ×10 <sup>-4</sup>	95.5
Pure water		$9.12(\pm 0.10) \times 10^{-4}$	91.2
Tap water (Tokat, Turkey)		9.02 (±0.13) ×10 <sup>-4</sup>	90.2

Table 3. Detection of Ba<sup>2+</sup> ion in different samples.

Comparison of the proposed new sensor with its counterparts in the literature is given in Table 4. As seen there, the sensor has a faster response time than previously proposed ones. It is relatively similar to the others in terms of linear working range and detection limit. When pH working ranges are examined, there is only one equivalent that can work at high pH levels independently of changes in the pH (Saleh, 2000).

Ionophore	Concentration range, M	Limit of detection, M	pH working range	Response time (s)	Reference
(E)-2-(2-((2- carbamothioylhydrazono)methyl)phenoxy)acetic acid	1.0×10 <sup>-6</sup> – 1.0×10 <sup>-1</sup>	5.54×10 <sup>-7</sup>	6.0-9.0	<10	Altunoluk et al., 2024
2,3,4-pyridine-1,3,5,7,12- pentaazacyclopentadeca-3-ene	$1.41 \times 10^{-6} - 1.0 \times 10^{-1}$	Not reported	2.5-7.0	18	Singh et al., 2005
4-4'-methylenediantipyrine	1.0×10 <sup>-6</sup> – 1.0×10 <sup>-2</sup>	5.2×10 <sup>-7</sup>	3.4-10.6	15	Abedi et al., 2008
1,2-bis(diarylphosphine oxide) naphthalene	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	$5.0 \times 10^{-6}$	3.0-11.0	60	Saleh, 2000
Barium-Rose Bengal	5.0×10 <sup>-5</sup> – 1.0×10 <sup>-1</sup>	2.5×10 <sup>-6</sup>	4.5-10.0	20	Othman et al., 2006
4-aminobenzoic acid 2-diethylaminoethyl ester	1.0×10 <sup>-5</sup> – 1.0×10 <sup>-1</sup>	4.23×10 <sup>-6</sup>	5.0-11.0	8	This work

**Table 4.** The potentiometric performance characteristics of sensor compared with other proposed barium ISEs.

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## 4. CONCLUSION

ISEs have an essential place in electroanalytical chemistry due to their versatile applications. Features such as low cost, on-site analysis, ease of preparation and simple use distinguish ISEs from other costly analytical devices that require a laboratory. For many years, researchers have proposed sensors selective to many cationic and anionic species by taking advantage of these properties of potentiometric ISEs. They have significant advantages over other analytical techniques, especially in the detection of ionic species. In this study, 4-aminobenzoic acid 2diethylaminoethyl ester was utilized as an ionophore. The proposed novel barium-selective potentiometric electrode was found to have a wide concentration range, near-Nernstian response, and lower limit of detection. Additionally, the sensor had a wide pH working range and fast analysis time. Therefore, we can state that the proposed sensor is rapid, selective, economical and reproducible for the on-situ detection of barium ions. This electrode which was successfully applied to different real samples can be utilized as an alternative to the various other analytical methods in the analysis of barium ions.

# 5. CONFLICT OF INTEREST

The authors state that they have no conflict of interest to declare.

# 6. **REFERENCES**

- Abedi, M. R., & Zamani, H. A. (2008). Barium (II)-PVC membrane sensor based on 4-4'methylenediantipyrine as a neutral carrier. *Analytical Letters*, *41*(12), 2251-2266. https://doi.org/10.1080/00032710802238077
- Abu-Shawish, H. M., Ghalwa, N. A., Al-Kashef, I. D., Saadeh, S. M., & Almonem, K. I. A. (2020). Extraordinary enhancement of a 5-fluorouracil electrode by praepagen HY micellar solutions. *Microchemical Journal*, 152, 104316. <u>https://doi.org/10.1016/j.microc.2019.104316</u>
- Abu-Shawish, H. M., Almonem, K. I. A., Saadeh, S. M., & Al-Iham, W. S. (2016). Determination of haloperidol drug in ampoules and in urine samples using a potentiometric modified carbon paste electrode. *Measurement*, *78*, 180-186. https://doi.org/10.1016/j.measurement.2015.10.008
- Altunoluk, O. C., Özbek, O., Kalay, E., Tokalı, F. S., & Aslan, O. N. Surface characterization of barium (II)-selective potentiometric sensor based on a newly synthesized derivative molecule. *Electroanalysis*, e202300407. <u>https://doi.org/10.1002/elan.202300407</u>
- Ardianrama, A. D., Pradyasti, A., Woo, H. C., & Kim, M. H. (2020). Colorimetric sensing of barium ion in water based on polyelectrolyte-induced chemical etching of silver nanoprisms. *Dyes and Pigments*, 181, 108578. <u>https://doi.org/10.1016/j.dyepig.2020.108578</u>
- Berkel, C., & Özbek, O. (2024). Green electrochemical sensors, their applications and greenness metrics

used: A review. *Electroanalysis*, *36*(11) e202400286. <u>https://doi.org/10.1002/elan.202400286</u>

- Bisergaeva, R. A., & Sirieva, Y. N. (2020, November). Determination of calcium and magnesium by atomic absorption spectroscopy and flame photometry. In *Journal of Physics: Conference Series, 1691,* 012055. <u>https://doi.org/10.1088/1742-6596/1691/1/012055</u>
- Buck, R. P., & Lindner, E. (1994). Recommendations for nomenclature of ion-selective electrodes. *Pure and Applied Chemistry*, 66(12), 2527-2536. <u>https://doi.org/10.1351/pac199466122527</u>
- de Oliveira, W., de Carvalho, M. D. F. B., de Almeida, E., Menegario, A. A., Domingos, R. N., Brossi-Garcia, A. L., ... & Santelli, R. E. (2012). Determination of labile barium in petroleum-produced formation water using paper-based DGT samplers. *Talanta*, *100*, 425-431. https://doi.org/10.1016/j.talanta.2012.08.013
- Erol, S., Özel, A. D., Yilmaz, M., & Kiliç, E. (2009). New Silver Ion-selective PVC Membrane and Coated-Graphite Electrodes based on a Novel Calix|4| arene Derivative. *Reviews in Analytical Chemistry*, 28(1), 27-50. <u>https://doi.org/10.1515/REVAC.2009.28.1.27</u>
- Gad, S.C. (2014). Barium, Encyclopedia of Toxicology (3th Editon), 368–370. <u>https://doi.org/10.1016/B978-0-</u> 12-386454-3.00819-8
- Grajeda, B. A. G., Acosta, S. G. S., Aguila, S. A., Guevara, H. P., Díaz-García, M. E., Enríquez, A. C., & Campos-Gaxiola, J. J. (2017). Selective and colorimetric detection of Ba 2+ ions in aqueous solutions using 11mercaptoundecylphosphonic acid functionalized gold nanoparticles. *RSC Advances*, 7(50), 31611-31618. <u>https://doi.org/10.1039/c7ra03861e</u>
- Huelga-Suarez, G., Fernández, B., Moldovan, M., & Alonso, J. I. G. (2013). Detection of transgenerational barium dual-isotope marks in salmon otoliths by means of LA-ICP-MS. *Analytical and Bioanalytical Chemistry*, 405, 2901-2909. <u>https://doi.org/10.1007/s00216-012-6452-2</u>
- Isildak, Ö., & Özbek, O. (2021). Application of potentiometric sensors in real samples. *Critical Reviews in Analytical Chemistry*, *51*(3), 218-231. <u>https://doi.org/10.1080/10408347.2019.1711013</u>
- Kravchenko, J., Darrah, T. H., Miller, R. K., Lyerly, H. K., & Vengosh, A. (2014). A review of the health impacts of barium from natural and anthropogenic exposure. *Environmental geochemistry and health*, *36*, 797-814. <u>https://doi.org/10.1007/s10653-014-9622-7</u>
- Llugany, M., Poschenrieder, C., & Barceló, J. (2000). Assessment of barium toxicity in bush beans. *Archives* of Environmental Contamination and Toxicology, 39, 440-444. <u>https://doi.org/10.1007/s002440010125</u>
- Modi, R. P., Mehta, V. N., & Kailasa, S. K. (2014). Bifunctionalization of silver nanoparticles with 6mercaptonicotinic acid and melamine for simultaneous colorimetric sensing of Cr<sup>3+</sup> and Ba<sup>2+</sup> ions. Sensors and Actuators B: Chemical, 195, 562-571. https://doi.org/10.1016/j.snb.2014.01.059
- Othman, A. M., El-Shahawi, M. S., & Abdel-Azeem, M. (2006). A novel barium polymeric membrane sensor for selective determination of barium and sulphate ions based on the complex ion associate barium (II)–Rose

Bengal as neutral ionophore. *Analytica Chimica Acta*, 555(2), 322-328. <u>https://doi.org/10.1016/j.aca.2005.09.016</u>

- Ören, S., Özbek, O., & Isildak, Ö. (2024). The use of thiazole derivative molecules as sensor materials: Potentiometric determination of Cu (II) ions. *Vietnam Journal of Chemistry*, 62(4), 486-492. <u>https://doi.org/10.1002/vjch.202300295</u>
- Özbek, O., & Isildak, Ö. (2022). Potentiometric PVC membrane sensor for the determination of antiepileptic drug levetiracetam in pharmaceutical formulations. *ChemistrySelect*, *7*(3), e202103988. https://doi.org/10.1002/slct.202103988
- Özbek, O., Çetin, A., Koç, E., & Isildak, Ö. (2022a). Synthesis and sensor properties of a phenol derivative molecule: potentiometric determination of silver (I) ions. *Electrocatalysis*, 13(4), 486-493.
- Özbek, O., Gezegen, H., Cetin, A., & Isildak, Ö. (2022b). A potentiometric sensor for the determination of Pb (II) ions in different environmental samples. *ChemistrySelect*, 7(33), e202202494. https://doi.org/10.1002/slct.202202494
- Özbek, O. (2023). A potentiometric sensor for the determination of potassium in different baby follow-on milk, water, juice and pharmaceutical samples. *Journal of Food Composition and Analysis*, *115*, 104937. https://doi.org/10.1016/j.jfca.2022.104937
- Özbek, O., & Altunoluk, O. C. (2023). Recent advances in nanoparticle-based potentiometric sensors. *Advanced Sensor and Energy Materials*, *3*, 100087. https://doi.org/10.1016/j.asems.2023.100087
- Özbek, O., & Altunoluk, O. C. (2024). Potentiometric determination of the local anesthetic procaine in pharmaceutical samples. *Analytical Biochemistry*, 695, 115657. https://doi.org/10.1016/j.ab.2024.115657
- Özbek, O., Ugur, Ö. B., Ören, S., Gürdere, M. B., & Kocabas, S. (2024a). New solid state contact potentiometric sensor based on a thiosemicarbazone derivative molecule for determination of copper (II) ions in environmental samples. *Polyhedron*, *252*, 116878. <u>https://doi.org/10.1016/j.poly.2024.116878</u>
- Özbek, O., Altunoluk, O. C., & Isildak, Ö. (2024b). Surface characterization and electroanalytical applications of the newly developed copper (II)-selective potentiometric sensor. *Analytical Sciences*, *40*(1), 141-149. <u>https://doi.org/10.1007/s44211-023-</u> 00436-z
- Saleh, M. B. (2000). Neutral bidentate organophosphorus compounds as novel ionophores for potentiometric membrane sensors for barium (II). *Fresenius Journal* of *Analytical Chemistry*, *367*, 530-534. <u>https://doi.org/10.1007/s002160000374</u>
- Singh, A. K., Singh, R., Singh, R. P., & Saxena, P. (2005). Novel potentiometric sensor for monitoring barium (II) based on 2, 3, 4-pyridine-1, 3, 5, 7, 12pentaazacyclopentadeca-3-ene. *Sensors and Actuators B: Chemical*, *106*(2), 779-783. https://doi.org/10.1016/j.snb.2004.09.030
- Umezawa, Y., Buhlmann, P., Umezawa, K., Tohda, K., & Amemiya, S. (2000). Potentiometric Selectivity Coefficients of Ion-Selective Electrodes. Part I.

Inorganic Cations. *Pure Appl. Chem*, *72*, 1851-2082. <u>https://doi.org/10.1351/pac200072101851</u>

- Verma, S., Sharma, A. K., & Shukla, S. K. (2023). Selffuelled nickel oxide encapsulated sodium alginategrafted-polypyrrole for potentiometric sensing of lead ions. *Materials Science and Engineering: B*, 293, 116469. https://doi.org/10.1016/j.mseb.2023.116469
- Wu, Y., Qileng, A., & Bakker, E. (2023). Self-powered optical ion sensor array based on potentiometric probes coupled to electronic paper. Sensors and Actuators B: Chemical, 396, 134561. https://doi.org/10.1016/j.snb.2023.134561
- Zamani, H. A., Hamed-Mosavian, M. T., Aminzadeh, E., Ganjali, M. R., Ghaemy, M., Behmadi, H., & Faridbod, F. (2010). Construction of barium (II) PVC membrane electrochemical sensor based on 3-deoxy-d-erythrohexos-2-ulose bis (thiosemicarbazone) as a novel ionophore. *Desalination*, *250*(1), 56-61. https://doi.org/10.1016/j.desal.2009.09.014

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# Examining the Prediction of Vapor-Liquid Equilibria through Comparative Analysis: Deep Learning versus Classical Cubic and Associating Fluid Theory Approaches

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Abstract: Accurate vapor-liquid equilibria (VLE) calculations of carbon dioxide and hydrogen sulfide mixtures are critical to gas processing and the affordable, safe design of flow assurance technologies. Inaccurate VLE predictions can lead to inaccurate gas hydrate phase equilibria predictions and ensuing safety and economic risks. This research paper explores the potential incorporation of Deep Neural Networks (DNNs) to support conventional expert systems within the context of predicting VLE. It facilitates more flexible and data-driven approaches that are required due to the growing intricacy and dynamic character of chemical processes. Moreover, various cubic and non-cubic equation of state (EoS) models (such as SRK, PR, CPA, SAFT, and PC-SAFT) were also examined to compare predicted VLE for various mixtures of CO<sub>2</sub> and H<sub>2</sub>S. Prior to the comparison of DNN-predicted VLE with EOS models, binary interaction parameters were optimized for all EOS with the available experimental phase equilibria measurements. Model accuracies were compared and analyzed for various binary systems containing CO<sub>2</sub>/H<sub>2</sub>S + other associative and nonassociative components. The absolute average deviation in vapor and liquid phase composition/bubble pressure was calculated and compared for all five-state EOS with DNN predictions. The DNN and equation of states with BIP gave a reliable illustration of the phase behavior of CO<sub>2</sub>/H<sub>2</sub>S-containing systems compared to others as indicated by the lower AADP values. By contrasting the applied DNN model with conventional techniques, we explore the promising channel for future research directions and industry applications, as well as an opportunity for innovation and field advancement for modern expert systems.

**Keywords**: Cubic Equation of states, Deep Neural Network, Vapor-Liquid Equilibria, PC-SAFT EOS, Process Design.

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# **1. INTRODUCTION**

Vapor-liquid equilibria (VLE) calculations are of utmost importance in chemical industries, including separation, flow assurance,  $CO_2$  sequestration, acid gas capture using amines, and gas hydrate phase equilibria prediction. While VLE of mixtures comprising of simple non-polar molecules (e.g., small hydrocarbons) can be reasonably explained using traditional estimation techniques (e.g., cubic EoS), accurate prediction of phase behavior of polar associating molecules (e.g., water, alcohols, glycols) and acid gaseous species (e.g.,  $CO_2$ ,  $H_2S$ ) is very difficult because of complex molecular arrangements as dictated by the nature and number of associating sites on the molecule. Errors in predicting phase behavior of these associating systems can lead to faulty design of various unit operations. Accurate prediction of VLE for  $CO_2$  and  $H_2S$  gas mixture decides the

accuracy of the hydrate phase boundary and significant error in VLE may result in an inaccurate hydrate stability condition.

Various researchers have measured the VLE behavior of CO<sub>2</sub> and H<sub>2</sub>S containing systems, as summarized in Table S1-S2. For example, a systematic study of  $H_2S$  + hydrocarbon mixtures was carried out by Stamataki and Magoulas (Stamataki & Magoulas, 2000). They employed the Jhaveri and Youngren's volume translated (J-PR) Peng-Robinson EoS to investigate the phase equilibria and volumetric behavior of H<sub>2</sub>S containing systems (Jhaveri & Youngren, 1988). A comprehensive evaluation of H<sub>2</sub>S containing ternary and guaternary systems (with methane, ethane, propane, and CO<sub>2</sub>) was performed using cubic plus association EoS by Tzirakis et al. (Tzirakis et al., 2016). Additional reviews and analysis of thermophysical properties and VLE of pure and mixed systems can be obtained from the following studies (Azari et al., 2013; da Silva et al., 2018; Diamantonis et al., 2013; Espanani et al., 2016; Faúndez & Valderrama, 2013; Ghosh, 1999; Lee & Lin, 2007; Nasrifar & Tafazzol, 2010; Tzirakis et al., 2016; Young et al., 2018).

Expert systems increase the effectiveness, reliability, and safety of chemical engineering processes by utilizing state-of-the-art computational techniques and domainspecific knowledge. Expert systems have the ability to optimize chemical process operations by suggesting and implementing advanced control methods. They can be particularly useful in predicting VLE equilibrium by combining domain knowledge, thermodynamic models, and computational methods.

Recently, Deep Neural Networks (DNNs) have been applied to predict various VLE data sets over range of T, and P conditions (Azari et al., 2013; Carranza-Abaid et al., 2023; Del-Mazo-Alvarado & Bonilla-Petriciolet, 2022; Eze & Masuku, 2018; Kamari et al., 2020; Nguyen et al., 2007; Roosta et al., 2019; Sharma et al., 1999; Vaferi et al., 2018; Wu et al., 2015; Zarenezhad & Aminian, 2011). A DNN is trained on an extensive dataset obtained from chemical engineering scenarios as part of the standard technique. In order to produce more sophisticated and precise predictions, the trained model seeks to identify complex patterns and relationships within the data. The expert system's current knowledge base can be combined with DNN results, allowing rulebased reasoning and data-driven insights to work in harmony.

TensorFlow integrates the Keras library, which includes the Functional APIs for constructing complex Neural Network (NNs) in flexible and powerful ways. The Functional APIs have not been often studied or used in chemical processes like Vapor-Liquid Equilibrium (VLE) prediction. In the context of chemical processes, especially VLE prediction, we may come across situations where the input data includes a combination of several categories (e.g., molecular structures, thermodynamic

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parameters, etc.) In these circumstances, the Functional API's capacity to manage common layers and numerous inputs and outputs can be useful. In non-linear regression analysis, it is challenging to estimate the functional relationship between the multi-dimensional independent and target variables. With the availability of APIs through the modern libraries of neural networks, it is convenient to design, and train customized NNs for better prediction of target data. The models created using functional APIs are more flexible than sequential designs, especially when prediction of multiple outputs are required using multidimensional input features. Such models are guite suitable to work with shared layers, non-linear topologies, or multi-dimensional regression problems where the multiple output with different physical meanings depends on the same input dataset.

The measurement of vapor-liquid equilibria for multicomponent systems over a range of temperature and pressure conditions is a costly, time-consuming, and laborious task. Hence, the accurate estimation of VLE is of utmost importance for the accurate design of process equipment and chemical applications. Conventionally, the equation of state coupled with the flash algorithm is the most common technique to estimate phase equilibria and thermophysical properties. Over the past decades, there have been many attempts to accurately estimate the equilibrium properties of hydrocarbons with gases of acids as highlighted in the following studies (Diamantonis et al., 2013; Li, 2008; Li & Yan, 2009; Wong & Sandler, 1984). However, there is a need to compare all different EoS models to evaluate their effectiveness in predicting phase equilibria. The current study highlights the effectiveness of various EoS models such as Soave Redlich Kwong (SRK), Peng Robinson (PR), cubic plus association (CPA), Statistical Associating Fluid Theory (SAFT), and perturbed chain SAFT (PC-SAFT) for phase equilibria prediction with optimized binary interaction parameters. Moreover, a DNN model was also created by using functional APIs of Keras to predict the VLE of hydrogen sulfide and carbon dioxide-containing binary systems. The model can predict pressure and vapor phase mole fraction very close to their experimental values. Expert systems typically employ domain knowledge and rule-based procedures, but utilizing Keras' Functional API can enhance system performance, especially for applications that benefit from deep learning techniques. To compare the model accuracies EoS algorithm was implemented with a reliable multiphase flash algorithm for predicting VLE. Finally, VLE predictions utilizing DNN were compared with various EoS mentioned earlier.

# 2. METHODOLOGY

The significant breakthrough in the field of NN occurred with the concept of backpropagation that deal with the adjustment of weights while training a multi-layer NN for minimum prediction error (Li et al., 2012). Meanwhile, the implementation of deep learning became possible with the help of modern computing resources, like

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powerful machines, advanced algorithms, and availability of larger datasets. It served many disciplines and solved complex problems in computer vision, healthcare, stock trading, social networks, and real-world problems from numerous branches of engineering (Mahfooz et al., 2023; Mahfooz et al., 2022; Zhong et al., 2021). In chemical engineering, the use of DNN is highly valuable for solving complex problems. Some major applications of DNNs have been observed in certain areas like quality control, process modeling and control, predictive maintenance, material design, energy efficiency, flow

assurance, water treatment, etc. (Han et al., 2019; Han et al., 2023; Zhang & Zhang, 2022). While solving realworld chemical engineering problems, high-quality data, architecture of DNN, and a robust training implementation are among the crucial requirements of using a DNN. Multiple layers of interconnected nodes make up a DNN, which is often divided into three basic types: An input layer, single or numerous hidden layers, and an output layer (see Figure 1). The term "deep" refers to the availability of multiple hidden layers, which allows learning of complex data representations.



Figure 1. A generalized deep neural network structure.

Here, we have implemented a functional API for designing and training a DNN. It offers an adaptable approach to create neural network architectures by defining the connections between layers in a more evident and practical pattern. It is more flexible than its competitor i.e., the sequential approach for constructing neural networks. Functional API is useful for multi-model and multitask learning as it conveniently affords multiple input and output layers. This adaptability empowers to build intricate network structures that concurrently offers multiple predictions on diverse types of data. A mathematical representation for a simple DNN using the Functional API with one shared layer and one non-shared (specific) layer is provided below. This example considers a DNN with two branches of input data, one shared layer, and one specific layer:

#### **Input Layers:**

Input for the first branch:  $X_1$ Input for the second branch:  $X_2$ **Shared Layer:** Linear Transformation:  $Z_s = W_s \cdot X_1 + b_s$ 

# Activation Function: $A_s = g_s(Z_s)$ Specific Layer:

Linear Transformation:  $Z_n = W_n \cdot X_2 + b_n$ Activation Function:  $A_n = q_n (Z_n)$ 

Where,  $X_1$  and  $X_2$  are inputs for first and second branch, respectively.  $Z_s$  and  $A_s$  are the outputs of the shared layer after applying a linear transformation and the activation function. Similarly,  $Z_n$  and,  $A_n$  are the output of the specific layer after applying the linear transformation and the activation function.  $W_{s_r} b_{s_r} W_{n_r}$  and  $b_n$  represent the weights and biases for the shared and specific layers. Here,  $g_s$  and  $g_n$  represent the activation functions applied to the shared and specific layers, respectively. The shared layer is normally used for feature extraction and the specific layer is used for task-specific processing. The input data from branches are processed separately that allows for different data types to be processed differently in the network. A simplified block flow diagram representing DNN implementation is illustrated in Figure 2.



Figure 2. A block flow diagram representing DNN implementation.

Conventionally, VLE is predicted utilizing cubic EoS and statistical associating fluids theory models (such as SAFT and PC-SAFT). Among cubic EoS, the Redlich-Kwong equation was the first reported modification to original van der Waal EoS (vd-EoS). Redlich and Kwong (RK) modified the vd-EoS with a T-dependent energy-associated term 'a(T)' to correct the PVT properties of fluids (Redlich & Kwong, 1949). The RK-EoS equation is given in by Equation 1:

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)} \tag{1}$$

Where a, b and  $\alpha$  are described in Table S3.

To improve phase behavior calculations at higher T and P, Soave suggested the revision in the RK EoS by encompassing a more complicated T dependence term to the attraction parameter, as given in Equation 2 (Soave, 1972).

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$$
(2)

v is molar-volume

 $a \, \&^{b}$  are energy and volume parameters for SRK EoS

The detailed information about SRK EoS parameters is discussed in Table S3 (provided in supplementary information). Moreover, the SRK-EoS energy parameter (a) for mixture is estimated by utilizing Equation 3:

$$a = \sum_{i}^{c} \sum_{j}^{c} x_{i} x_{j} a_{ij}$$

and,

$$a_{i_j} = (1 - ki_j)(a_i a_j)^{0.5}$$
(3)

Furthermore, Peng and Robinson (1976) introduced an EoS by transforming the attractive term's denominator and developed a modified form for the EOS parameters (such as *a* and *b*), which offers additional benefits to the SRK-EOS in predicting liquids, as shown in Equation 4 (Peng & Robinson, 1976).

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$
(4)

(-)

Concerning non-cubic equation of states, Chapman et al. (Chapman et al., 1989) proposed a SAFT EoS model to estimate accurate fluid phase equilibria, established on the Statistical Associating Fluid Theory (SAFT). The SAFT-EoS can be expressed in terms of Helmholtz free energy (A) by the generalized form as described by Equation 5:

$$A^{res} = A^{seg} + A^{chain} + A^{Assos}$$
(5)

In contrast to SAFT, the PC-SAFT EoS regard molecules as chains consist of hard spherical-segments, and the effect of chain-length is considered for both repulsive and dispersive contributions. Moreover, the PC-SAFT EoS also considers the association term is to account for, and model systems containing polar organic molecules ( $H_2S$ ,  $CO_2$ ), organic hydrate inhibitors (alcohols, glycols), hydrocarbons (low to medium hydrocarbon) and water. (Gross & Sadowski, 2001). The PC-SAFT EoS is implemented in the current work for various binary systems of  $H_2S/CO_2$  + hydrocarbon and given by Equation 6.

(6)

$$A^{res} = A^{seg} + A^{chain} + A^{Assos}$$

Cubic plus association (CPA) EoS is an expansion of SRK EoS with an additional term for the association of molecules and is given by Equation 7.

 $A(T,V,n) - A^{IGM}(T,V,n) = \Delta A^{phy} + \Delta A^{Assos}$ (7) where,  $A^{phy}$  is the Helmholtz free energy (A) contribution term which considered the variation due to the presence of repulsive and attractive interactions and  $A^{Assos}$  is the Helmholtz free energy term that account for the changes in A because of association of molecules.

The  $A^{phy}$  and  $A^{Assos}$  term of the CPA equation of state is given in (Equations 8 & 9) (Soave, 1972).

$$\Delta A^{phy} = n\left(-\log\left(1 - \frac{b_m}{V}\right) - \frac{a_m}{RTb_m}\log\left(1 + \frac{b_m}{V}\right)\right)$$
(8)

$$\Delta A^{assos}(T,V,n) = nRT\sum_{S} \left(\ln X + \frac{1-X}{2}\right)$$

Expt. & optimization

Moreover, the  $X^A$  which is defined as the fraction of species not bonded at site A, and is calculated by (Equation 10) (Chapman et al., 1989; Huang & Radosz, 1991).

$$X^{A} = \left(1 + \rho \sum_{B} X^{B} \Delta^{AB}\right)^{-1}$$
(10)

The  $X^{A}$  for mixtures is calculated by utilizing Equation (11):

$$X_{A_{i}} = \frac{1}{1 + \rho \sum_{j} x_{j} \sum_{B_{j}} X_{B_{j}} \Delta^{A_{i}B_{j}}}$$
(11)

A generalized algorithm representing optimization of pure component and binary interaction parameters for numerous fluid phase models is illustrated in Figure 3. Additional details and parameters used in above mentioned EoS are provided in the supplementary materials (Equations S1-S12).



(9)

Figure 3. A generalized algorithm illustrating VLE prediction and model parameters (BIP & pure component) optimization using equation of states.

# **3. EXPERIMENT AND RESULTS**

## 3.1. Data for Vapor Liquid Equilibria

Nevertheless, to achieve erroneous prediction of vaporliquid equilibria using DNN and equation of states (both cubic and non-cubic EOS), vapor-liquid equilibria experimental data was also collected over a wide range of pressure, temperature, and compositions. Tables S1 & S2 enlist the VLE experimental measurements for various binary mixtures of hydrogen sulfide and carbon dioxide in the presence of hydrocarbons. The collection of thermodynamically corrected data is essential as any

source of unreliable data sets may lead to model inaccuracies. The current data set is adapted from Khan et al. (2016)(Khan et al., 2016). The experimental dataset will ensure the accurate optimization of binary interaction parameters before the prediction of phase envelopes utilizing cubic and non-cubic equations of state. The absolute average deviation in predicting pressure and compositions is entirely dependent on the goodness of experimental data as the coupled uncertainties may result in error-based prediction.

#### Naveed Khan et al., (2025), 8(1), 11-28. **3.2. Deployment of DNN to Estimate Fluid Phase** Equilibria

The imprecise knowledge of VLE becomes critical for the operation and control of chemical processes. The predictions with thermodynamics models often show deviation from the experimental VLE data and some exclusively data-driven models with their parameter fitting approach may not exactly specify data-fitting function. Moreover, these models normally use iterative algorithms with significant computational cost. A neural network model trained on a dataset, can efficiently predict better results, and can be integrated with any existing software packages for data evaluations. Figure 4 shows the architecture of the designed neural network model that is constructed by utilizing TensorFlow and functional APIs of Keras (Abadi et al., 2016).



Figure 4. VLE neural network for prediction of pressure (P) and vapor phase composition (y).

As demonstrated in Figure 4, the computational model of neural network establishes a relationship between input features and outputs that are available at two different ends of the network. The first hidden layer is connected to the first output layer and second hidden layer. However, the second output layer then follows the second hidden layer. The first hidden layer is a shared layer that finds joint features advantageous to each of the two outputs. In contrast, the second hidden layer improves prediction accuracy by learning specific features for predicting the second output. The proposed architecture is quite suitable for multi-dimensional regression problems, where multiple output with different physical meanings depends on the same input dataset.



Figure 5. Comparison plot for AI trained predicted Pressure (P) and experimental pressure.

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Our binary VLE data include molar fractions of components, temperature, pressure, and critical properties of components. The data were divided randomly into training (60%), validation (20%), and test (20%) datasets. The validation and test datasets are utilized for assessing the overall efficiency of the network. Feature scaling was also applied to preprocess the raw dataset. It confirms about the contribution of each feature is proportionately equal for the predictions and the model is trained accurately and efficiently. Our scaled features ( $x_i$ ) are obtained by using standardization of input values (x) as given below by Equation 12:

$$x_{i} = \frac{x - mean(x)}{standard \, deviation(x)}$$
(12)

A neural network can approximate any function by minimizing a cost function using backpropagation or gradient descent (Hanin, 2019; Hornik, 1991; Irie & Miyake, 1988; Nasrifar & Tafazzol, 2010). The performance of neural network is measured at each learning step by observing the cost function. We used Mean Square Error (MSE) for training our model that is the most common cost function for the regression problems. It is defined as given by Equation 13:

$$MSE = \frac{1}{N} \sum_{i=1}^{N} (y_i - \hat{y}_i)^2$$
(13)

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Here, N represents the # of observations in the given input dataset. The actual and evaluated output values are represented by  $y_i$  and  $\hat{y}_i$  respectively.

Hyperparameters were optimized after very keen observations at different stages of model design. One of the objectives was to produce a model that avoids overadaption of training data and generalizes well on new data. This issue of memorization of training data by complex models is known as overfitting that always limits the generalization of any model. Early stopping is one of the techniques to overcome this issue. We applied early stopping by choosing a patience value of 20, that means training is stopped if there is no improvement over validation set for 20 consecutive epochs. To achieve better performance of optimization, we used Nadam (Nesterov-accelerated Adaptive Moment Estimation) that is an extension of the famous Adam optimizer (Tato & Nkambou, 2018). The optimizer algorithms help to achieve reduction in cost function that keep changing the weights and learning rate of the neural network. The default value of learning rate was used to initialize the training. Figures 5 & 6 compares the predicted values of P and y with their values measured experimentally. All points are close to the regressed diagonal line showing satisfactory results achieved by the model. In addition, the absolute average deviation in pressure and vapor phase (AADP/AADy %) mole fraction calculated utilizing the DNN for  $H_2S$  and  $CO_2$  containing binary systems as represented in Figure 7 & 8 respectively. The calculated AADP/AADy using the trained model were tested for 20% of the total datasets. The model on the basis of individual critical parameters, liquid phase mole fraction, and temperature accurately output the vapor phase mole fraction and pressure.



Figure 6. Comparison plot for AI trained predicted vapor phase mole fraction and experimental vapor phase mole fraction.



**Figure 7.** Absolute average deviation in pressure and vapor phase mole fraction (AADP/AADy %) Using AI trained network for various CO<sub>2</sub> containing binary systems.



**Figure 8.** Absolute average deviation in pressure and vapor phase mole fraction (AADP/AADy %) Using AI trained network for various H<sub>2</sub>S containing binary systems.

# 3.3. Vapor-Liquid Equilibria using Cubic Equation of States

The flash algorithm was coupled with cubic and non-cubic EoS to calculate VLE for numerous  $H_2S$  and CO2-containing binary systems. Prior to the prediction of VLE

utilizing EoS, binary interaction parameters were optimized to account for the interaction between the species. Figure 9 (a) shows predicted VLE utilizing the PR EoS for  $CO_2$ + n- $C_7$  binary mixtures over a range of T & P.



Figure 9. Model predictions for (a) CO<sub>2</sub>+ n-C<sub>7</sub> over a T range of 310.65 to 394.26 K (b) H<sub>2</sub>S + cyclohexane over a T range of 323.15 to 422.60 K (c)  $H_2S$  + n-C<sub>6</sub> vapor-liquid equilibria over a T range of 322.9 to 422.6 K and (d)  $H_2S$  +  $n-C_7$  over a temperature range of 310.92 to 477.594 K VLE using the PR EoS. Experimental measurements were taken from (Kalra et al., 1978; Laugier & Richon, 1995; Ng et al., 1980; Théveneau et al., 2006).

Figure 9 (b) represents the VLE predictions compared measurements with experimental for H<sub>2</sub>S + cyclohexane binary mixtures over a T range of 323.15 to 422.60 K. The model estimations agree well with the experimental measurements. Nevertheless, the pressure-composition envelop predictions start deviating from experimental data within proximity of the critical point. The inaccuracy in predicting vapor-liquid equilibria near critical regions may be associated with the version of the a function. Hence, to accurately predict the phase envelop near-critical region, it is suggested here to test the PR-EOS with various correlations available for a calculation as discussed in detail by the following researchers (Dahl & Michelsen, 1990; Lopez-Echeverry et al., 2017; Mathias & Copeman, 1983; Twu et al., 2002a). The a function shows linearly dependency on temperature in the supercritical region and thus it is recommended (Twu et al., 2002b) to utilize the second function when temperature exceeds the critical point.

(Lopez-Echeverry et al., 2017). It is quite apparent from Figure 9 (c-d) that the PR EoS predictions of VLE for binary mixtures of  $H_2S + n-C_7/n-C_6/cyclohexane$  over a range of temperatures and pressures show reasonably fair agreement in the dew and bubble point calculations. The calculations illustrate that the model successfully predicts binary systems VLE, and a temperaturedependent binary interaction parameter (BIP) is essential to precisely estimate the liquid part of the phase envelope. Conclusively, the PR EoS precisely predicts the phase envelope for selected self-associating systems. The predicted phase envelopes utilizing Peng Robinson EoS for all other binary systems also show reasonable accuracy with experimental measurements (see Section 3.5 for comparison and Table S6 for a summary of results without BIP).

However, the former modification may result in

implications are discussed in detail in the following study

and

the

a discontinuity in enthalpy calculation,



**Figure 10**. Model predictions for (a)  $CO_2$ + n- $C_7$  over a T range of 310.65 to 394.26 K (b)  $H_2S$  + n-hexane over a T range of 322.9 K to 422.6 K (c)  $H_2S$  + n- $C_7$  vapor-liquid equilibria over a T range of 310.92 K to 477.594 K vapor-liquid equilibria utilizing the SRK EoS. Experimental measurements were taken from (Kalra et al., 1978; Laugier & Richon, 1995; Ng et al., 1980; Théveneau et al., 2006).

Similarly, to evaluate the effectiveness of SRK EoS, an algorithm was developed, and T- dependent BIP was optimized for CO<sub>2</sub> and H<sub>2</sub>S binary mixtures. The SRK EoS predictions for binary systems such as  $CO_2+n-C_7$  and H<sub>2</sub>S +  $n-C_6/n-C_7$  are also in reasonable agreement with the experimental measurements, as shown in Figure 10 (a-c). However, as evident from Figure 10 (c), the SRK predictions are accurate at low to moderate temperatures but show deviation at higher temperatures for the liquid part illustrating the importance of the SAFT-based equation of state.

The CPA EoS incorporates the association term in its formulation to account for the hydrogen bonding in associative molecules. Hence, it provides a significant improvement over SRK EoS for VLE prediction. Figure 11 (a-c) indicates that the CPA EoS predictions of VLE for H<sub>2</sub>S + n-C<sub>6</sub>/n-C<sub>7</sub>/cyclohexane binary mixture over a T range of 310.92 to 422.6 K. It is apparent from Figure 11 (a) that the CPA EoS model is successful in capturing liquid and vapor side phase boundary for H<sub>2</sub>S (self-association) + non-associative systems; hence illustrating the reliability of this CPA EoS.



**Figure 11**. CPA EoS predictions for (a)  $H_2S + n-C_6$  over a T range of 322.90 to 422.6 K (b)  $H_2S + n-C_7$  over a T range of 310.92 K to 422.6 K (c)  $H_2S +$  cyclohexane over a T range of 323.15 K to 422.6 K. Experimental data was taken from (Laugier & Richon, 1995; Ng et al., 1980; Théveneau et al., 2006).

Figures 11 (b-c) shows the evaluation of CPA-EOS model predictions for the  $H_2S$  + n-C<sub>7</sub>/cyclohexane binary systems VLE over a *T* range of 310.92 to 422.6 K. VLE predictions for  $H_2S$  + n-C<sub>7</sub>/cyclohexane systems agree with the experimental measurements, except immediate to the critical point at moderately higher T. The significant errors in calculating dew and bubble point P at

higher T are credited to the range of  $T_r$  over which the CPA-EOS parameters were optimized (CPA EoS parameters were optimized up to a  $T_r$  range of 0.90). **3.4. PC-SAFT Predictions for VLE of H<sub>2</sub>S/CO<sub>2</sub>** 

In addition, to evaluating the effectiveness of the non-cubic EoS, VLE predictions were also carried out using SAFT-EOS and its modification (PC-SAFT).





**Figure 12.** Model prediction for (a) H<sub>2</sub>S + cyclohexane (b) H<sub>2</sub>S + nC<sub>6</sub> and (c) H<sub>2</sub>S + n-C<sub>7</sub> VLE using SAFT (statistical associating fluid) EoS. Experimental measurements were taken from (Laugier & Richon, 1995; Ng et al., 1980; Théveneau et al., 2006).

Prior to VLE calculation using SAFT EoS, binary interaction parameters were optimized utilizing carefully selected experimental data. Pure component parameters (three parameters for non-associative species (such as hydrocarbons) and 2 parameters for associating species) for SAFT were adopted from the literature (see Table S5). Figures 12 (a-c) demonstrate the dew and bubble point calculations for  $H_2S$  + n-Cyclohexane/n-C<sub>6</sub>/n-C<sub>7</sub> binary mixtures. The VLE calculations are in reasonable accord with the experimental data, but the liquid part of the VLE envelope was slightly overpredicted by the SAFT-EoS. The model predictions for the selected binaries show excellent accord for the vapor part of the phase envelope, yet the VLE envelope's liquid part is slightly overpredicted. Also, it is not unusual to have wrong predictions of thermophysical properties and VLE envelopes utilizing inappropriate pure components and BIP. The uncertainties in prediction near far critical regions and the liquid part of the envelop might be associated with the poorly optimized equation of state parameters.

The higher-order SAFT EoS (Chapman et al., 1990; Wertheim, 1984) was modified to develop PC-SAFT (Gross & Sadowski, 2001; Huang & Radosz, 1990, 1991). PC-SAFT-EoS originated from SAFT, as in SAFT, the reference fluid is considered a hard sphere whereas PC-SAFT uses a hard chain. The PC-SAFT EoS contemplates molecules as chains consisting of hard spherical segments, and the effect of chain length is considered for both repulsive and dispersive contributions as discussed in Section 2. In this work, the PC-SAFT EoS algorithm was adapted from (Martín et al., 2011) and parameters used are listed in Table S4.



**Figure 13.** Model predictions for (a)  $H_2S + n-C_6 \&$  (b)  $H_2S + n-C_7$  VLE utilizing the PC SAFT EoS. Experimental measurements were taken from(Laugier & Richon, 1995; Ng et al., 1980; Théveneau et al., 2006).

The VLE predictions of  $CO_2$  + n- $C_{10}$  / predictions utilizing PC-SAFT with optimized binary methylcyclohexane binary mixtures reveal that model interaction parameters are in excellent accord with

experimental measurements (Figure S5 a-b). The VLE calculations were also conducted for the CO<sub>2</sub> + n-C<sub>7</sub> binary mixture as given in Figure S1. The PC-SAFT predictions are observed to be more precise for the vapor part of the VLE envelope in comparison with the liquid part; the latter was slightly under-predicted by PC-SAFT EoS in all the former binary mixtures (see Table S7 for a summary). The higher error in the liquid part of the phase envelope utilizing SRK-EOS is attributed to the inherent limitation of accurately predicting liquid densities. In contrast, Peng & Robinson's Equation of state shows reasonably better prediction because of the term b(v-b), which significantly improves the depiction of the attractive part of the equation of state, and consequently, improves the ability of the PR-EOS to predict liquid densities. Also, Figures 13 (a-b) show VLE predictions and experimental measurements for H<sub>2</sub>S+n- $C_6/n-C_7$  binary systems over a range of T and P. It is quite evident from Figure 13 (a-b) that PC-SAFT predictions are in close accord with experimental measurements. Figure S6 compares the errors in predicting the bubble pressure for binary systems of H<sub>2</sub>S &  $CO_2$  using the SAFT and PC-SAFT EoS. PC-SAFT EoS was observed to provide equivalent precision to SAFT in predicting the vapor phase. However, PC-

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SAFT EoS gives overall improved prediction in estimating the bubble pressure (see Figure S6(a-b). A summary of DNN and five EoS in predicting VLE of  $CO_2$  and  $H_2S$  containing binary mixtures is also discussed in Section 3.4.

# **3.5.** Comparisons of DNN and EoS Models for VLE Prediction

To examine the effectiveness of DNN over cubic and noncubic EoS in the prediction of VLE of binary systems, errors in predicted P and vapor phase composition (y) are compared. Before comparing the performance of the various equations of state models, all the experimental data points were utilized in optimizing the binary interaction parameter as per the below objective functions.

$$AADP = \frac{1}{N} \sum_{i=1}^{N} \frac{P_{\exp} - P_{calc}}{P_{\exp}} * 100\%$$
(14)

As expected, the cubic equation and non-cubic EoS show drastic improvements in prediction accuracy when binary interaction parameters are carefully optimized (see also summary in Table S6 & Table S7 for comparison).



Figure 14. Comparison of AADP % for H<sub>2</sub>S containing binary mixtures.

Figure 14-15 compares the absolute average deviation in vapor phase compositions and pressures (AADy % & AADP %) prediction for DNN with cubic and SAFT-based EOS with optimized BIP. Based on the optimized binary interaction parameters for various multicomponent systems the calculated AADx/AADy and AADp enlisted in Figures 14 &15 for all equation of state (cubic and non-cubic) models. Additionally, to celebrate the impact of BIP optimization, the un-optimized VLE predictions using cubic and SAFT-based models are given in Tables S6 & S7. The hydrogen sulfide-containing systems including binary mixtures of  $H_2S+C_4$ ,  $H_2S+i-C_4$ ,  $H_2S+C_5$ ,  $H_2S+C_6$ ,  $H_2S+C_7$ ,  $H_2S+cyclohexhane, and$ 

H<sub>2</sub>S+Ethylcyclohexane, shows that the PC-SAFT EOS output least error (0.975% for *AAdy* and 1.420 % for *AADp* respectively). Moreover, the PC-SAFT equation of state also shows accurate predictions accuracy for CO<sub>2</sub>-containing binary mixtures, and the binary mixture of CO<sub>2</sub>+N<sub>2</sub>, CO<sub>2</sub>+C<sub>6</sub>, CO<sub>2</sub>+C<sub>8</sub>, CO<sub>2</sub>+Cyclohexane, CO<sub>2</sub>+C<sub>6</sub>H<sub>6</sub>, CO<sub>2</sub>+C<sub>10</sub>, CO<sub>2</sub>+C<sub>7</sub>, and CO<sub>2</sub>+Toluene shows an absolute error of 1.48 % and 2.97 % for *AAdy* and *AADp* respectively. A comparison of the CPA equation of state provides an average error in predicting y & x is to be 2.51 % & 5.96 % respectively for H<sub>2</sub>S-containing gas mixtures and an error of 2.57 % and 17.26 % for CO<sub>2</sub>-

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containing gas mixtures. By contrast, the trained model (DNN) predicted higher accuracy for all selected binary systems and the average error in predicting yand P is 5.20 % & 6.04 % respectively for binary CO<sub>2</sub> mixtures. Moreover, the trained DNN model also shows reasonable error in predicting yand P to be 4.46 % & 6.35 % respectively for H<sub>2</sub>S-containing gas mixtures. Overall, a relative comparison of VLE prediction shows that PC SAFT EOS yielded the least deviation in comparison with other equation of state models. However, the DNN model

developed in this work is comparable to cubic and SAFTbased EoS. Designed DNN shows acceptable accuracy in predicting phase equilibria for various  $H_2S$  and  $CO_2$  binary systems over an extended range of T and P conditions. It was also observed that the execution of flash calculation utilizing DNN does not need long computational time even if coupled with the dynamic process simulation. In contrast, non-cubic equations of states (SAFT and PC-SAFT) and CPA EoS require higher computational time when coupled with the dynamic process simulation.



Figure 15. Comparison of AADP % for CO<sub>2</sub> containing binary mixtures.

## 4. CONCLUSION AND FUTURE DIRECTIONS

The DNNs have remarkable abilities to capture complex, nonlinear correlations that are inherent in VLE systems. By using data-driven learning, the model can replace traditional methods for prediction, especially in scenarios where there are intricate interactions between multiple variables. The functional APIs have been underexplored in constructing NNs for chemical processes. They have potential to enable the expert system to integrate deep learning models and harness the power of neural networks used in chemical engineering processes. By using a DNN model through functional APIs, multiple parameters along with VLE data were included in training data sets over range of T and P conditions. Cubic, SAFT, and PC-SAFT EoS were tested to predict VLE of H2S/CO<sub>2</sub> containing binary mixtures. Absolute errors were estimated and compared with results obtained using the developed DNN model for various binary mixtures, including self-associating systems. The model was compared with EoS predictions utilizing optimized binary interaction parameters and provided comparable accuracy as PC-SAFT EoS (most accurate among the 5 EoS tested in this work). However, time required for flash calculation using DNN was significantly lower than SAFT, PC-SAFT, and CPA EoS. This warrants further evaluation of DNN-based approach as lower computational time along with VLE prediction accuracy comparable to PC-SAFT could be of significant interest to process simulation software developers. While, predicting the vapor part of the phase envelope, all equation of states including DNN give reasonable accuracy. However, the liquid part of the phase envelope's predictions shows significant errors using all EoS, mainly because of the poorly fitted association EoS terms for these systems.

- I. The Soave Redlich Kwong and Peng Robinson equation of states should be tested with various forms of a function to completely test the accuracy of the cubic equation of states.
- II. Over the past decades multiple formulations for  $a \wedge b$  were proposed in the cubic equation of state to improve saturation pressure, liquid density, and VLE predictions. Thus, it would be recommended to thoroughly test those formulations to select optimal parameters.
- III. In addition to the testing of basic parameters in cubic equations of states, various combinations of repulsive and attractive terms should also be tested comprehensively to estimate accurate VLE and thermophysical properties.
- IV. The use of conventional and unconventional mixing rules in all equations of states should be tested extensively to locate the most suitable way to estimate a multi-component system.
- V. Generally, binary interaction parameters were optimized utilizing experimental VLE data, however, there is a need to estimate binary

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# **5. REFERENCES**

- Abadi, M., Agarwal, A., Barham, P., Brevdo, E., Chen, Z., Citro, C.,...Devin, M. (2016). Tensorflow: Large-scale machine learning on heterogeneous distributed systems. *arXiv preprint arXiv:1603.04467*.
- Azari, A., Atashrouz, S., & Mirshekar, H. (2013). Prediction the vapor-liquid equilibria of CO2containing binary refrigerant mixtures using artificial neural networks. *International Scholarly Research Notices*, 2013.
- Carranza-Abaid, A., Svendsen, H. F., & Jakobsen, J. P. (2023). Thermodynamically consistent vaporliquid equilibrium modelling with artificial neural networks. *Fluid Phase Equilibria*, *564*, 113597.
- Chapman, W. G., Gubbins, K. E., Jackson, G., & Radosz, M. (1989). SAFT: equation-of-state solution model for associating fluids. *Fluid Phase Equilibria*, *52*, 31-38.
- Chapman, W. G., Gubbins, K. E., Jackson, G., & Radosz, M. (1990). New reference equation of state for associating liquids. *Industrial & Engineering Chemistry Research*, 29(8), 1709-1721.
- da Silva, V. M., do Carmo, R. P., Fleming, F. P., Daridon, J.-L., Pauly, J., & Tavares, F. (2018). High pressure phase equilibria of carbon dioxide+ n-alkanes mixtures: Experimental data and modeling. *Fluid Phase Equilibria*, *463*, 114-120.
- Dahl, S., & Michelsen, M. L. (1990). High-pressure vapor-liquid equilibrium with a UNIFAC-based equation of state. *AIChE journal*, *36*(12), 1829-1836.
- Del-Mazo-Alvarado, O., & Bonilla-Petriciolet, A. (2022). Assessment of the simultaneous regression of liquid-liquid and vapor-liquid equilibria data of binary systems using NRTL and artificial neural networks. *Fluid Phase Equilibria*, 561, 113537.
- Diamantonis, N. I., Boulougouris, G. C., Mansoor, E., Tsangaris, D. M., & Economou, I. G. (2013). Evaluation of cubic, SAFT, and PC-SAFT equations of state for the vapor-liquid equilibrium modeling of CO2 mixtures with other gases. *Industrial & Engineering Chemistry Research*, *52*(10), 3933-3942.
- Espanani, R., Miller, A., & Jacoby, W. (2016). Prediction of vapor-liquid equilibria for mixtures of low boiling point compounds using Wong-Sandler mixing rule and EOS/GE model. *Chemical Engineering Science*, *152*, 343-350.
- Eze, P. C., & Masuku, C. M. (2018). Vapour–liquid equilibrium prediction for synthesis gas conversion using artificial neural networks. *South African journal of chemical engineering*, 26(1), 80-85.
- Faúndez, C. A., & Valderrama, J. O. (2013). Modeling associating hydrocarbon+ alcohol mixtures using the Peng-Robinson equation of state and

the Wong-Sandler mixing rules. *Comptes Rendus Chimie*, *16*(2), 135-143.

- Ghosh, P. (1999). Prediction of vapor-liquid equilibria using peng-robinson and soave-redlich-kwong equations of state. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 22(5), 379-399.
- Gross, J., & Sadowski, G. (2001). Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Industrial & Engineering Chemistry Research*, 40(4), 1244-1260.
- Han, X., Zhang, L., Zhou, K., & Wang, X. (2019). ProGAN: Protein solubility generative adversarial nets for data augmentation in DNN framework. *Computers & chemical engineering*, 131, 106533.
- Han, Y., Du, Z., Geng, Z., Fan, J., & Wang, Y. (2023). Novel long short-term memory neural network considering virtual data generation for production prediction and energy structure optimization of ethylene production processes. *Chemical Engineering Science*, *267*, 118372.
- Hanin, B. (2019). Universal function approximation by deep neural nets with bounded width and relu activations. *Mathematics*, *7*(10), 992.
- Hornik, K. (1991). Approximation capabilities of multilayer feedforward networks. *Neural networks*, 4(2), 251-257.
- Huang, S. H., & Radosz, M. (1990). Equation of state for small, large, polydisperse, and associating molecules. *Industrial & Engineering Chemistry Research*, *29*(11), 2284-2294.
- Huang, S. H., & Radosz, M. (1991). Equation of state for small, large, polydisperse, and associating molecules: extension to fluid mixtures. *Industrial & Engineering Chemistry Research*, 30(8), 1994-2005.
- Irie, & Miyake. (1988). Capabilities of three-layered perceptrons. IEEE 1988 international conference on neural networks,
- Jhaveri, B. S., & Youngren, G. K. (1988). Threeparameter modification of the Peng-Robinson equation of state to improve volumetric predictions. *SPE reservoir engineering*, *3*(03), 1033-1040.
- Kalra, H., Kubota, H., Robinson, D. B., & Ng, H.-J. (1978). Equilibrium phase properties of the carbon dioxide-n-heptane system. *Journal of chemical and Engineering Data*, 23(4), 317-321.
- Kamari, E., Hajizadeh, A. A., & Kamali, M. R. (2020). Experimental investigation and estimation of light hydrocarbons gas-liquid equilibrium ratio in gas condensate reservoirs through artificial neural networks. *Iranian Journal of Chemistry* and Chemical Engineering (IJCCE), 39(6), 163-172.
- Khan, M. N., Warrier, P., Peters, C. J., & Koh, C. A. (2016). Review of vapor-liquid equilibria of gas hydrate formers and phase equilibria of

Naveed Khan et al., (2025), 8(1), 11-28. hydrates. *Journal of Natural Gas Science and Engineering*, *35*, 1388-1404.

- Laugier, S., & Richon, D. (1995). Vapor-liquid equilibria for hydrogen sulfide+ hexane,+ cyclohexane,+ benzene,+ pentadecane, and+(hexane+ pentadecane). *Journal of chemical and Engineering Data*, 40(1), 153-159.
- Lee, M.-T., & Lin, S.-T. (2007). Prediction of mixture vapor–liquid equilibrium from the combined use of Peng–Robinson equation of state and COSMO-SAC activity coefficient model through the Wong–Sandler mixing rule. *Fluid Phase Equilibria*, 254(1-2), 28-34.
- Li, H. (2008). Thermodynamic properties of CO2 mixtures and their applications in advanced power cycles with CO2 capture processes KTH].
- Li, H., & Yan, J. (2009). Evaluating cubic equations of state for calculation of vapor–liquid equilibrium of CO2 and CO2-mixtures for CO2 capture and storage processes. *Applied Energy*, *86*(6), 826-836.
- Li, J., Cheng, J.-h., Shi, J.-y., & Huang, F. (2012). Brief introduction of back propagation (BP) neural network algorithm and its improvement. Advances in Computer Science and Information Engineering: Volume 2,
- Lopez-Echeverry, J. S., Reif-Acherman, S., & Araujo-Lopez, E. (2017). Peng-Robinson equation of state: 40 years through cubics. *Fluid phase equilibria*, 447, 39-71.
- Mahfooz, S., Alhasani, A., & Hassan, A. (2023). SDG-11.6. 2 Indicator and Predictions of PM2. 5 using LSTM Neural Network. 2023 1st International Conference on Advanced Innovations in Smart Cities (ICAISC),
- Mahfooz, S., Ali, I., & Khan, M. N. (2022). Improving stock trend prediction using LSTM neural network trained on a complex trading strategy. *International Journal for Research in Applied Science and Engineering Technology*, 10(7), 4361-4371.
- Martín, Á., Bermejo, M. D., Mato, F. A., & Cocero, M. J. (2011). Teaching advanced equations of state in applied thermodynamics courses using open source programs. *Education for Chemical Engineers*, 6(4), e114-e121.
- Mathias, P. M., & Copeman, T. W. (1983). Extension of the Peng-Robinson equation of state to complex mixtures: Evaluation of the various forms of the local composition concept. *Fluid phase equilibria*, *13*, 91-108.
- Nasrifar, K., & Tafazzol, A. H. (2010). Vapor– liquid equilibria of acid gas– aqueous ethanolamine solutions using the PC-SAFT equation of state. *Industrial & Engineering Chemistry Research*, 49(16), 7620-7630.
- Ng, H.-J., Kalra, H., Robinson, D. B., & Kubota, H. (1980). Equilibrium phase properties of the toluene-hydrogen sulfide and heptane-hydrogen sulfide binary systems. *Journal of chemical and Engineering Data*, *25*(1), 51-55.

# **RESEARCH ARTICLE**

- Nguyen, V. D., Tan, R. R., Brondial, Y., & Fuchino, T. (2007). Prediction of vapor–liquid equilibrium data for ternary systems using artificial neural networks. *Fluid Phase Equilibria*, 254(1-2), 188-197.
- Peng, D.-Y., & Robinson, D. B. (1976). A new twoconstant equation of state. *Industrial & Engineering Chemistry Fundamentals*, 15(1), 59-64.
- Redlich, O., & Kwong, J. (1949). On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. *Chemical Reviews*, 44(1), 233-244.
- Roosta, A., Hekayati, J., & Javanmardi, J. (2019). Application of artificial neural networks and genetic programming in vapor–liquid equilibrium of C 1 to C 7 alkane binary mixtures. *Neural Computing and Applications*, *31*, 1165-1172.
- Sharma, R., Singhal, D., Ghosh, R., & Dwivedi, A. (1999). Potential applications of artificial neural networks to thermodynamics: vapor–liquid equilibrium predictions. *Computers & chemical engineering*, 23(3), 385-390.
- Soave, G. (1972). Equilibrium constants from a modified Redlich-Kwong equation of state. *Chemical Engineering Science*, *27*(6), 1197-1203.
- Stamataki, S., & Magoulas, K. (2000). Prediction of phase equilibria and volumetric behavior of fluids with high concentration of hydrogen sulfide. *Oil & Gas Science and Technology*, *55*(5), 511-522.
- Tato, A., & Nkambou, R. (2018). Improving adam optimizer.
- Théveneau, P., Coquelet, C., & Richon, D. (2006). Vapour–liquid equilibrium data for the hydrogen sulphide+ n-heptane system at temperatures from 293.25 to 373.22 K and pressures up to about 6.9 MPa. *Fluid phase equilibria*, 249(1-2), 179-186.
- Twu, C. H., Sim, W. D., & Tassone, V. (2002a). An extension of CEOS/AE zero-pressure mixing rules for an optimum two-parameter cubic equation of state. *Industrial & Engineering Chemistry Research*, 41(5), 931-937.
- Twu, C. H., Sim, W. D., & Tassone, V. (2002b). Getting a handle on advanced cubic equations of state. *Chemical engineering progress*, 98(11), 58-65.
- Tzirakis, F., Karakatsani, E., & Kontogeorgis, G. M. (2016). Evaluation of the cubic-plus-association equation of state for ternary, quaternary, and multicomponent systems in the presence of monoethylene glycol. *Industrial & Engineering Chemistry Research*, 55(43), 11371-11382.
- Vaferi, B., Lashkarbolooki, M., Esmaeili, H., & Shariati, A. (2018). Toward artificial intelligence-based modeling of vapor liquid equilibria of carbon dioxide and refrigerant binary systems. *Journal* of the Serbian Chemical Society, 83(2), 199-211.

- Wertheim, M. S. (1984). Fluids with highly directional attractive forces. I. Statistical thermodynamics. *Journal of statistical physics*, *35*(1-2), 19-34.
- Wong, D. S., & Sandler, S. I. (1984). Calculation of vapor-liquid-liquid equilibrium with cubic equations of state and a corresponding states principle. *Industrial & engineering chemistry fundamentals*, 23(3), 348-354.
- Wu, Y., Kowitz, C., Sun, S., & Salama, A. (2015). Speeding up the flash calculations in two-phase compositional flow simulations–The application of sparse grids. *Journal of Computational Physics*, 285, 88-99.
- Young, A. F., Magalhães, G. D., Pessoa, F. L., & Ahón, V. R. (2018). Vapor-liquid equilibrium of binary systems with EoS/GE models at low pressure: Revisiting the Heidemann-Kokal Mixing Rule. *Fluid Phase Equilibria*, 466, 89-102.
- Zarenezhad, B., & Aminian, A. (2011). Predicting the vapor-liquid equilibrium of carbon dioxide+ alkanol systems by using an artificial neural network. *Korean Journal of Chemical Engineering*, 28, 1286-1292.
- Zhang, K., & Zhang, H. (2022). Predicting solute descriptors for organic chemicals by a deep neural network (DNN) using basic chemical structures and a surrogate metric. *Environmental Science & Technology*, *56*(3), 2054-2064.
- Zhong, S., Zhang, K., Wang, D., & Zhang, H. (2021). Shedding light on "Black Box" machine learning models for predicting the reactivity of HO radicals toward organic compounds. *Chemical Engineering Journal*, 405, 126627.

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# Removal of Cadmium from Aqueous Solutions using Nickel Hydroxide/Reduced Graphene Oxide Composite: Response Surface Methodology Optimization and Nonlinear Isotherm Modeling

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**Abstract**: Removal of Cd(II) ions from aqueous solutions was investigated using a nickel hydroxide/reduced graphene oxide composite as the adsorbent material. Influential parameters of the batch adsorption process were optimized using the Box-Behnken design, which enabled a systematic evaluation of the effects of various factors. An analysis of variance was performed to develop a quadratic regression model for predicting the percentage of Cd(II) removal. The optimal conditions for achieving maximum removal efficiency were identified as an adsorbent dosage of 60 mg, a pH of 8.0, and a mixing period of 40 minutes. Isotherm analysis was conducted using nonlinear regression, with the sum of squared errors serving as the error function. The results indicated that the Langmuir model provided a better fit to the experimental data compared to the Freundlich model, as evidenced by higher determination coefficients (0.9684) and lower error values. This suggested that the adsorption process is characterized by a monolayer adsorption mechanism on a homogeneous surface. The maximum adsorption capacity was found to be 218 mg/g, indicating the effectiveness of the nickel hydroxide/reduced graphene oxide composite in removing Cd(II) ions from solution.

Keywords: Cadmium, Metal oxide, Graphene Oxide, Adsorption Isotherms, Nonlinear Regression.

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# **1. INTRODUCTION**

Release of heavy metals into aquatic significant environments has become а environmental concern due to their persistent and toxic nature. Unlike organic pollutants, heavy metals do not degrade and can accumulate in ecosystems, posing long-term threats to both the environment and human health. Cadmium (Cd), a particularly hazardous heavy metal, is extensively used in industries such as battery manufacturing, electroplating, textile processing, pesticides, dyes and plastic production. The ongoing industrial activity involving Cd-containing products significantly impacts the environment, leading to increased

Cd levels and high exposure risks to human health (Charkiewicz et al., 2023).

In recent years, extensive research has focused on the biological effects of Cd, which is classified as a toxic and carcinogenic substance, with the potential to stimulate various harmful biological processes. Cd tends to accumulate predominantly in the kidneys and liver, each storing about 30%, while the rest is dispersed across other organs. This accumulation is concerning due to its exceptionally long biological half-life, which can extend from 10 to 30 years (Peana et al., 2023). The accumulation of Cd in various tissues causes the disruption of key cellular processes like proliferation and differentiation, and triggers oxidative stress by

promoting the formation of reactive oxygen species. Prolonged exposure to Cd causes longterm damage in the body, weakens bones, contributes to cardiovascular problems and increases the risks of cancers in the lungs, prostate and other organs (Hayat et al., 2019) (Gulisano et al., 2009). Because of its toxic effects, the removal of cadmium from environmental sources is critical to prevent contamination of water bodies.

A range of treatment technologies such as ionexchange processes, electrochemical methods and chemical precipitation have been employed for the removal of heavy metals from water bodies (Goyal et al., 2021; Hosseini et al., 2020; Kim et al., 2024; Pohl, 2020; Sun et al., 2020; Zhang & Duan, 2020). However, adsorption has emerged as a favored approach due to its economic viability, ease of operation, and ability to effectively handle trace amounts of metal contaminants. The initial step in an adsorption process is to select the most suitable adsorbent based on factors such as the adsorption capacity, uptake rate, production cost, and the type of adsorbate (Saleem et al., 2019). Currently, there is a significant demand for engineered nanomaterials characterized by highly porous structures and large surface area properties, as the potential candidates in heavy metal removal. Metal oxides such as iron oxide (Gusain et al., 2024), manganese oxide (Peng et al., 2015), aluminum oxide (Sen & Sarzali, 2008), zinc oxide (Sharma et al., 2019); carbon nanomaterials such as carbon nanotube (Al-Khaldi et al., 2015), graphene/graphene oxide (Bian et al., 2015), graphitic carbon nitride (Guo et al., 2018); and their combinations (Liu et al., 2016; Thy et al., 2019) have attracted considerable attention to remove Cd from aqueous systems. Metal oxides exhibit high adsorption capacities attributed to their large surface areas, high binding affinities and tunability of active surface sites (Gupta et al., 2021). However, reducing the size of metal oxides to the nanometer scale leads to a significant increase in surface energy, which compromises their stability. This instability often leads to aggregation driven by interparticular forces like Van der Waals interactions and reduces their effectiveness in adsorption processes (Hua et al., 2012). Graphene-based nanomaterials can serve as effective porous supporting materials to minimize aggregation and enhance the mechanical integrity and scalability of metal oxides. Due to the challenges and high costs associated with the large-scale synthesis of graphene-based nanomaterials, embeddina them into metal oxides offers a more economically viable solution (Gupta et al., 2021; Sreeprasad et al., 2011).

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Despite the extensive literature on the adsorption of Cd using metal oxide and carbon nanomaterials, there is limited research specifically focused on their combined effects. This gap in research highlights the need for further exploration into the development of hybrid material, as they possess unique properties that could improve their adsorption capacity in heavy metal removal from water systems. For example, metal oxides can be produced by cost-effective routes, regenerated through simple methods and exhibit good chemical stability across a wide range of pH levels (Kumar et al., 2013). On the other hand, graphene-based nanomaterials offer numerous active sites with an exceptional surface area and porous structure, making them particularly efficient in removing pollutants from contaminated water (Dayana Priyadharshini et al., 2022).

In this study, nickel hydroxide and graphene oxide were selected to synthesize the hybrid material due to their complementary properties potential for enhanced adsorption and performance. Nickel hydroxide is well-known for its high adsorption capacity, surface reactivity, and chemical stability, making it an effective material for removing pollutants from aqueous systems (Ogata et al., 2016; Zheng et al., 2021). As the second constituent of the composite, graphene oxide exhibits abundant functional groups oxygen-containing that facilitate the adsorption and improve the dispersion of the hybrid material. Previous studies have demonstrated the efficacy of similar hybrid materials for the removal of Cd ions from aqueous solutions (Deng et al., 2013; Wan et al., 2018).

Herein, nickel hydroxide/reduced graphene oxide [Ni(OH)<sub>2</sub>/RGO] composite was synthesized via a straightforward method and employed for the efficient removal of cadmium ions from solutions. aqueous Batch adsorption experiments were systematically conducted, with key experimental parameters optimized using Response Surface Methodology (RSM) to enhance adsorption efficiency. In adsorption studies, RSM enables analysis of the influence of variables and their interactions, allowing for precise predictions of adsorption behavior. This methodology reduces the number of required experiments, thereby saving time and costs, while also identifying the most influential parameters and enhancing the understanding of process dynamics (Anfar et al., 2020). The equilibrium adsorption data obtained under optimum conditions were evaluated by fitting them to both Langmuir and Freundlich isotherm utilizing models. non-linear rearession techniques to assess the adsorption behavior and model suitability.

#### 2. EXPERIMENTAL SECTION

#### 2.1. Chemicals and Reagents

All reagents used were of analytical grade, and ultrapure water from a Healforce Smart Mini system was used to prepare all samples and standard solutions. A Cd(II) stock solution (1000 mg/L) was obtained from High Purity Standards (North Charleston, USA), and daily working and calibration solutions were freshly diluted from the stock solution. Nickel nitrate [Ni(NO<sub>3</sub>)<sub>2</sub>], ammonium fluoride (NH<sub>4</sub>F), and ammonium hydroxide (NH<sub>4</sub>OH), essential for synthesizing Ni(OH)<sub>2</sub> nanoflowers, and other reagents used in synthesis of graphene oxide such as hydrogen peroxide, 35% hydrochloric acid, 95-98% sulfuric acid, 85% orthophosphoric acid, hydrazine hydrate, potassium permanganate were all purchased from Merck (Darmstadt, Germany). Nitric acid (65% v/v), purchased from Isolab (Germany), and used as the eluent. Buffer solutions at pH 4 and 6 were prepared using potassium dihydrogen phthalate (Merck, Germany), while the pH 8 buffer solution was prepared using sodium tetraborate decahydrate (Merck, Germany). Graphite powder with a high purity of 99.9995% was supplied from Alfa Aesar.

#### 2.1. Synthesis Procedure

The synthesis of Ni(OH)<sub>2</sub>/RGO composites followed a procedure adapted from the literature, employing а homogeneous precipitation technique (Cheng et al., 2010). Initially, graphene oxide (GO) was synthesized graphite powder using Improved from Hummer's method (Marcano et al., 2010). For the synthesis of Ni(OH)<sub>2</sub>/RGO composites, 100 mg of GO was dispersed in 250 mL of deionized water through ultrasonication for 1.0 h. The homogeneous dispersion of GO was then added to the nickel precursor solution, which was prepared by dissolving 3.5 g of Ni(NO<sub>3</sub>)<sub>2</sub> and 1.5 g of NH<sub>4</sub>F in 250 mL of deionized water. Ammonium hydroxide solution was then added dropwise to the mixture until the pH was adjusted to 8.0. Following this, 100  $\mu L$  of hydrazine hydrate was introduced to the mixture for the in-situ reduction of graphene oxide. The resulting solution was heated to 60 °C and stirred continuously for 40 minutes. Afterward, the mixture was filtered, and the particles were thoroughly washed with water and ethanol. Finally, the product was dried in an oven at 55 °C for 24 hours.

#### 2.2. Instrumentation

The concentration of Cd in aqueous solutions was determined using a ATI UNICAM 929 AA model Flame Atomic Absorption Spectrophotometer (FAAS). The hollow cathode lamb of cadmium (Varian, USA) was operated with a wavelength of 228.2 nm, 0.50 nm spectral bandpass and 12.0 mA. A deuterium

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lamp was used for the correction of background. The Raman spectrum of Ni(OH)<sub>2</sub>/RGO composite was recorded using an inVia Renishaw Raman spectrometer with a 532 nm laser beam. SEM images were captured with a FEI Quanta 600 scanning electron microscope (SEM). Prior to imaging, the nanoparticle surfaces were coated with gold-palladium using a Quorum SC7620 Sputter Coater under argon plasma.

#### 2.2. Batch Study

Adsorption experiments were conducted in 10.0 mL of aqueous solution containing different concentrations of Cd (II). 1.0 mL of pH 8.0 buffer and 60.0 mg of Ni(OH)<sub>2</sub>/RGO composite were added to the Cd containing solutions. The solutions were agitated on an orbital shaker for at room temperature. After 40.0 minutes, individual flasks were removed and the upper phase transferred to conical tubes for centrifugation at 5000 rpm for 5 minutes. Finally, the solutions were sent to FAAS for the determination of Cd(II) concentration. The following equations (Eq. 1 and 2) were used to calculate the removal and adsorption rates of Cd(II).

$$Q = \frac{(C_0 - C_i)xV}{m}$$
 (Eq. 1)

$$%RE = \frac{(C_0 - C_i) \times 100}{C_0}$$
 (Eq. 2)

where Q refers to the adsorption capacity of composite material in mg/g, %RE is the removal percentage of Cd(II) ions, V is the solution volume in L, m is the adsorbent amount in g,  $C_i$  and  $C_0$  are the Cd(II) concentration at final and initial stage in mg/L.

#### 2.3. Response Surface Methodology

Box-Behnken design, as part of Response Surface Methodology (RSM), was applied to determine the optimum conditions for the adsorption process. The experimental setup involved three factors: Adsorbent dosage (A), pH (B) and mixing period (C), each evaluated at three levels (-1, 0, 1), as detailed in Table 1. A quadratic polynomial equation was used to model the experimental data, and the corresponding regression coefficients were calculated. The general form of non-linear quadratic equation is described in Equation 3 (Dean et al., 2017).

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i=1}^n \sum_{j=1}^n \beta_{ij} x_i x_j + \varepsilon$$
(Eq. 3)

where the term  $\beta_0$  denotes to the model coefficient while  $\beta_{i}$ ,  $\beta_{ii}$ ,  $\beta_{ii}$  correspond to the

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linear, quadratic, and interaction coefficients, respectively. The variables  $x_i$  and  $x_j$  are the independent factors in their coded levels, n is the number of independent variables, and  $\varepsilon$  is the model error. The dependent variable

represents the removal percentage of Cd(II) ion. The ranges of values for the factors in the experimental design were determined based on preliminary experiments and practical considerations relevant to the adsorption process.

		Factor 1	Factor 2	Factor 3
Std	Run	A:Adsorbent dosage, mg	B:pH	C:Mixing period, min
11	1	40	4.0	40
13	2	40	6.0	21
5	3	5.0	6.0	2.0
12	4	40	8.0	40
16	5	40	6.0	21
8	6	75	6.0	40
10	7	40	8.0	2.0
6	8	75	6.0	2.0
4	9	75	8.0	21
14	10	40	6.0	21
17	11	40	6.0	21
7	12	5.0	6.0	40
3	13	5.0	8.0	21
1	14	5.0	4.0	21
9	15	40	4.0	2.0
2	16	75	4.0	21
15	17	40	6.0	21

Table 1: The values of variables in experimental design.

#### 2.4. Adsorption Isotherm Models

Langmuir and Freundlich models were used to analyze the adsorption equilibrium data. The model equations of Langmuir and Freundlich in their non-linear forms are described in Equation 4 and 5, respectively (Al-Ghouti & Da'ana, 2020).

$$Q_e = \frac{b Q_m C_e}{1 + b C_e}$$
 (Eq. 4)

$$Q_e = K C_e^n \tag{Eq. 5}$$

In Equation 4,  $C_e$  is the equilibrium concentration of Cd(II) in mg/L, while  $Q_e$  is the adsorbed amount of Cd(II) in mg/g. The maximum adsorption capacity of adsorbent and the adsorption energy are denoted by  $Q_m$  (mg/g) and b (L/mg), respectively. In Equation 5, K (mg/g (L/mg)<sup>1/n</sup>) and n (dimensionless) are the Freundlich constants. Here, n indicates how well the adsorption process conforms to the model, while K represents the amount of Cd(II) adsorbed per unit equilibrium concentration on the adsorbent material.

In the non-linear approach, error analysis was performed using Solver add-in function in Microsoft Excel. The error function, the sum of the square of the errors (ERRSQ), was minimized to achieve the best fit between the experimental data and the estimated model predictions. The ERRSQ equation is presented as follows (Suwannahong et al., 2021):

$$ERRSQ = \sum_{i=1}^{n} \left( Q_{e,experimental} - Q_{e,predicted} \right)^{2}$$

(Eq. 6)

The coefficient of determination  $(R^2)$  was investigated as an indicator of model suitability. The value of  $R^2$  ranges from 0 to 1, with higher values indicating a better model fit. The formula for  $R^2$  as follows (Suwannahong et al., 2021):

$$R^{2} = 1 - \frac{\sum_{i=1}^{n} (Q_{e,experimental} - Q_{e,predicted})^{2}}{\sum_{i=1}^{n} (Q_{e,experimental} - \overline{Q_{e,experimental}})^{2}}$$
(Eq. 7)

## **3. RESULTS AND DISCUSSION**

#### 3.1. Characterization

The morphological characterization of the Ni(OH)<sub>2</sub>/RGO composite was examined using SEM analysis. The SEM image of the composite, shown in Figure 1, revealed cube-like structures of Ni(OH)<sub>2</sub> randomly distributed across the RGO sheets (Vivek et al., 2023). The FTIR spectrum of composite is displayed in Figure 2. The sharp peak at 3625 cm<sup>-1</sup> was attributed to the O-H stretching vibrations, confirming the O-H bonds in beta nickel hydroxide and the presence of

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water molecules adsorbed between layers (Akhtar et al., 2024). The weak bands around 2900 cm<sup>-1</sup> and 1048 cm<sup>-1</sup> were associated with the asymmetric and symmetric CH<sub>2</sub> stretching and C-O-C stretching vibrations, respectively, corresponding to the remaining oxygen-containing functionalities in GO structure after reduction (Emiru & Ayele, 2017). Additionally, the characteristic band centered at 556 cm<sup>1</sup> was assigned to the stretching vibrations of Ni-OH (Şaylan et al., 2022). These findings confirm the incorporation of RGO into the nickel hydroxide lattice.



Figure 1: SEM image of Ni(OH)<sub>2</sub>/RGO composite.



Figure 2: FTIR spectrum of Ni(OH)<sub>2</sub>/RGO composite.

#### 3.2. Analytical Parameters of Cd(II) Determination

The analytical parameters of Cd(II) determination was evaluated through the limit of detection (LOD), limit of quantification (LOQ), repeatability (percent relative standard deviation, %RSD), linear range and regression analysis. The different concentrations of Cd(II) (0.10-10.0 mg/L) were prepared from the stock solution by diluting with ultrapure water. This calibration standards were analyzed by FAAS and the lowest concentration with a signal/noise ratio equal or greater than 3 was used to determine LOD and LOQ values for Cd(II) **RESEARCH ARTICLE** 

determination. The following equations (Eq. 8 and 9) were used to LOD and LOQ values.

$$LOD = 3 xS/m$$
 (Eq. 8)

$$LOQ = 10 xS/m$$
 (Eq. 9)

where S is the standard deviation of at least five replicate analyses of lowest concentration and m is the slope of calibration plot constructed in the linear range. The linear range was determined as the range with a  $R^2 \ge 0.99$ . The analytical parameters of Cd(II) determination is given in Table 2.

**Table 2:** The analytical parameters of Cd(II) determination by FAAS.

Parameter	Value
LOD, mg/L	0.021
LOQ, mg/L	0.072
%RSD	6.5
Linear range, mg/L	0.10 - 5.0
R <sup>2</sup>	0.9919

The method demonstrated LOD and LOQ values of 0.021 mg/L and 0.072 mg/L, respectively. Satisfactory repeatability was achieved, with an %RSD of 6.5% at the lowest concentration level. The linear range was established between 0.10 and 5.0 mg/L, with an R<sup>2</sup> value of 0.9919. Effluent and influent concentrations during the adsorption process were determined using the linear equation from the calibration plot (y = 0.0685x + 0.01). Samples with concentrations exceeding the linear range were appropriately diluted before analysis.

## 3.3. RSM Modelling

The experimental design for the optimization of operating conditions in the batch adsorption process was developed using Box-Behnken design. The effects of independent variables [adsorbent dosage (A), pH (B) and mixing period (C)] on the removal percentage of Cd(II) from aqueous solutions were investigated based on the analysis of variance (ANOVA). Table 3 represents the ANOVA results of experimental design.

Table 3: Analysis of variance for the experimental design of adsorptive removal of Cd(II).

Source	Sum of	df	Mean	F-value	p-value	
Model	7173	6	1195	52.1	5.7E-07	significant
A-Adsorbent dosage	2033	1	2033	88.6	2.76E-06	
В-рН	4221	1	4221	184	9.17E-08	
C-Mixing period	257	1	257	11.21	0.0074	
AB	202	1	202	8.81	0.0141	
AC	127	1	127	5.51	0.0408	
B <sup>2</sup>	333	1	333	14.53	0.0034	
Residual	229	10	22.9			
Lack of Fit	189	6	31.4	3.08	0.1477	not significant
Pure Error	40.8	4	10.2			
Cor Total	7402	16				
R <sup>2</sup>	0.9690					
Adjusted R <sup>2</sup>	0.9504					
Predicted R <sup>2</sup>	0.8619					
Adeq Precision	25.32					

The results given in Table 3 demonstrated a strong model fit, with a highly significant pvalue (p < 0.0001) and an insignificant lack of fit. This indicated that the chosen variables were well-suited for the model, accurately the experimental data representing and confirming its reliability for predicting response values. The robustness of the model was further validated by a high R<sup>2</sup> value of 0.9690, which was close to 1.00, indicating a good fit to the experimental data and strong predictive power. In addition to that, the satisfactory alignment between the predicted R<sup>2</sup> (0.9504) and adjusted R<sup>2</sup> (0.8619) showed the reliability of model, confirming the minimal overfitting and consistent performance in predicting and adjusting the datasets (Roy et al., 2014).

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The independent variables, adsorbent dosage, pH and mixing period, were found to be significant factors in the adsorption process. Significant interaction effects were observed between adsorbent dosage and pH, as well as adsorbent dosage and mixing period, indicating that these variables influence each other's effect on adsorption efficiency. Furthermore, the quadratic term for pH revealed a non-linear relationship, showing the importance of optimizing pH for maximum adsorption. The response surface graphs showing the removal percentage as a function of the interactions between the two variables are illustrated in Figure 3. In this analysis, the two parameters were varied while the other was held constant.



**Figure 3:** 3D response surface plots for Cd(II) removal percentage for the interaction between two operating parameters.

As seen in Figure 3, the removal percentage of Cd(II) increased with the increase in adsorbent dosage, likely due to the increase in the presence of active sites. pH was identified as the most influential factor in the removal of Cd(II) ions. The removal efficiency increased significantly, from 20% to 91%, as the pH of solution was increased from 4 to 8. This improvement was attributed to the formation of favorable conditions for electrostatic attraction between the negatively charged adsorbent surface and positively charged Cd(II) ions at higher pH levels (Lin et al., 2018). The highest cadmium removal was observed at pH 8. To assess the potential for Cd(II) ion precipitation as hydroxides, control experiments were conducted with Cd(II) spiked samples at a fixed

without concentration. the addition of adsorbent. The absorbance values of Cd(II) solution in ultrapure water were compared with those at pH 8.0, and the reduction in absorbance was used as an indicator of Cd(II) precipitation. Results showed that only about 12% of Cd(II) was converted into hydroxides, suggesting that the conditions did not lead to significant precipitation. This finding supports the conclusion that adsorption, rather than precipitation, was the primary removal mechanism for Cd(II) in this study.

The quadratic model used to predict the removal percentage (%RE) of Cd(II) from aqueous solutions using Ni(OH)<sub>2</sub>/RGO composite is expressed in Equation 10.

 $\% RE = 57.2362 - 0.3315 A - 19.1913 B - 0.03979 C + 0.101557 AB + 0.008457 AC + 2.2178 B^{2}$  (10)

As a result, the optimum conditions of the batch adsorption process were determined to be an 60 mg of adsorbent dosage, pH 8.0 and a

mixing period of 40 minutes. The average removal percentage of Cd(II) under optimum conditions was calculated as %93.

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# 3.4. Isotherm analysis by nonlinear regression

A nonlinear approach was applied to analyze the adsorption data using Langmuir and Freundlich isotherm models. Error analyses were performed to estimate isotherm parameters with ERRSQ employed as the error function to be minimized. The estimated parameters of adsorption isotherms are presented in Table 4.

**Table 4:** The isotherm parameters of Langmuir and Freundlich models estimated by nonlinear regression.

	Parameter	Value
	Q <sub>m</sub> (mg/g)	218.12
	b (L/mg)	0.2418
Langmuir	R <sup>2</sup>	0.9684
	ERRSQ	132.8
	K (mg/g) (L/mg) <sup>1/n</sup>	40.83
Eroundlich	n	0.775
Freuhalich	R <sup>2</sup>	0.9487
	ERRSQ	215.9

As given in Table 4, the adsorption data analysis indicated that the Langmuir model provided a better fit than the Freundlich model for Cd(II) adsorption. The maximum adsorption capacity  $(Q_m)$  was found to be 218.12 mg/g, suggesting a high adsorption potential, while the Langmuir indicated moderate affinity constant (b) between the adsorbent and adsorbate ions (Al-Ghouti & Da'ana, 2020). A high correlation coefficient ( $R^2$ =0.9684) and lower error sum of squares (ERRSQ=132.8) further confirmed the suitability of the Langmuir model, suggesting monolayer adsorption on a homogeneous surface (Ncibi, 2008). In comparison, the lower R<sup>2</sup> and higher ERRSQ for Freundlich revealed that it was less effective in representing the adsorption behavior accurately.

The performance of the synthesized hybrid material was compared with similar adsorbents reported in the literature, particularly graphene oxide/metal oxide nanocomposites for Cd removal. For example, magnetic graphene oxide demonstrated a maximum adsorption capacity of 91.29 mg/g (Deng et al., 2013), while reduced graphene oxide-zinc oxide nanocomposites achieved 49.99 mg/g for the removal of Cd(II) from contaminated wastewater (Motitswe et al., 2024). Similarly, magnetic iron oxide/graphene oxide ( $Fe_3O_4/GO$ ) nanocomposites exhibited а maximum adsorption capacity of 52.083 mg/g for Cd(II) removal (Thy et al., 2019). Furthermore, in another study, the maximum adsorption capacity was reported as 45.05 mg/g using a magnetic graphene oxide/MgAI-layered double hydroxide nanocomposite for cadmium in aqueous solutions during batch equilibrium experiments (Huang et al., 2018). In terms of adsorption behavior, magnetic graphene oxide (Deng et al., 2013) and magnetic iron oxide/graphene oxide nanocomposites (Thy et al., 2019) also followed the Langmuir model, with electrostatic interactions and surface functional groups playing a significant role in

adsorption. In contrast, reduced graphene oxide-zinc oxide nanocomposites (Motitswe et 2024) exhibited a combination of al.. heterogeneous and homogeneous coverage, with adsorption mechanisms attributed to ionic bonding and dipole-dipole interactions involving oxygen groups on ZnO nanoparticle. Huang et al. (2018) identified multiple mechanisms, including surface complexation, precipitation of metal hydroxides, and isomorphic replacement, for Cd(II) adsorption on MgAl-layered double hydroxides, while the Langmuir model was also observed (Huang et al., 2018). Overall, while diverse mechanisms and adsorption behaviors were reported across these studies, the high adsorption capacity and strong interactions observed in this study revealed the potential of the Ni(OH)<sub>2</sub>/RGO composite as an effective adsorbent for Cd(II) removal from aqueous environments.

# 4. CONCLUSION

In this study, the adsorption of Cd(II) ions from aqueous solutions using Ni(OH)<sub>2</sub>/RGO composite was investigated for the efficient removal of this element. The effects of mixing period, pH and adsorbent dosage were examined to achieve maximum adsorption efficiency. Response surface methodology using Box-Behnken design was employed to optimize the influential parameters. pH of solution and adsorbent dosage were identified as key parameters influencing Cd(II) removal. The adsorption isotherm analysis was performed using nonlinear regression analysis. The Langmuir model provided the best fit, with an R<sup>2</sup> value close to 1 and low value of error function. This finding suggested monolayer adsorption on a uniform surface with finite adsorption sites, indicative of a strong, specific interaction between the adsorbent and Cd(II) ions. With a high maximum adsorption capacity of 218 mg/g, the Ni(OH)<sub>2</sub>/RGO composite demonstrates
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considerable potential as an effective material for Cd(II) removal in aqueous environments.

## **5. CONFLICT OF INTEREST**

The author declares that she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## 6. REFERENCES

- Akhtar, M. S., Wejrzanowski, T., Komorowska, G., Adamczyk-Cieślak, B., & Choinska, E. (2024). Microwave-assisted hydrothermal synthesis of  $\alpha\beta$ -Ni(OH)2 nanoflowers on nickel foam for ultrastable electrodes of supercapacitors. Electrochimica Acta, 508, 145284. https://doi.org/https://doi.org/10.1016/j.e lectacta.2024.145284
- Al-Ghouti, M. A., & Da'ana, D. A. (2020). Guidelines for the use and interpretation of adsorption isotherm models: A review. Journal of Hazardous Materials, 393, 122383.
- Al-Khaldi, F. A., Abu-Sharkh, B., Abulkibash, A. M., & Atieh, M. A. (2015). Cadmium removal by activated carbon, carbon nanotubes, carbon nanofibers, and carbon fly ash: a comparative study. Desalination and Water Treatment, 53(5), 1417–1429.
- Anfar, Z., Ait Ahsaine, H., Zbair, M., Amedlous, A., Ait El Fakir, A., Jada, A., & El Alem, N. (2020). Recent trends on numerical investigations of response surface methodology for pollutants adsorption onto activated carbon materials: A review. Critical Reviews in Environmental Science and Technology, 50(10), 1043– 1084.
- Bian, Y., Bian, Z.-Y., Zhang, J.-X., Ding, A.-Z., Liu, S.-L., & Wang, H. (2015). Effect of the oxygen-containing functional group of graphene oxide on the aqueous cadmium ions removal. Applied Surface Science, 329, 269–275.
- Charkiewicz, A. E., Omeljaniuk, W. J., Nowak, K., Garley, M., & Nikliński, J. (2023). Cadmium Toxicity and Health Effects—A Brief Summary. In Molecules (Vol. 28, Issue 18). https://doi.org/10.3390/molecules281866 20
- Cheng, Z., Xu, J., Zhong, H., Li, D., Zhu, P., & Yang, Y. (2010). A facile and novel

#### **RESEARCH ARTICLE**

synthetic route to Ni(OH)2 nanoflowers. Superlattices and Microstructures, 48(2), 154–161. https://doi.org/https://doi.org/10.1016/j.s pmi.2010.05.013

- Dayana Priyadharshini, S., Manikandan, S., Kiruthiga, R., Rednam, U., Babu, P. S., Subbaiya, R., Karmegam, N., Kim, W., & Govarthanan, M. (2022). Graphene oxide-based nanomaterials for the treatment of pollutants in the aquatic environment: Recent trends and perspectives - A review. Environmental Pollution, 306, 119377. https://doi.org/https://doi.org/10.1016/j.e nvpol.2022.119377
- Dean, A., Voss, D., Draguljić, D., Dean, A., Voss, D., & Draguljić, D. (2017). Response surface methodology. Design and Analysis of Experiments, 565-614.
- Deng, J.-H., Zhang, X.-R., Zeng, G.-M., Gong, J.-L., Niu, Q.-Y., & Liang, J. (2013). Simultaneous removal of Cd(II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent. Chemical Engineering Journal, 226, 189-200. https://doi.org/https://doi.org/10.1016/j.c ej.2013.04.045
- Emiru, T. F., & Ayele, D. W. (2017). Controlled synthesis, characterization and reduction of graphene oxide: A convenient method for large scale production. Egyptian Journal of Basic and Applied Sciences, 4(1), 74–79.
- Goyal, P., Tiwary, C. S., & Misra, S. K. (2021). Ion exchange based approach for rapid and selective Pb (II) removal using iron oxide decorated metal organic framework hybrid. Journal of Environmental Management, 277, 111469.
- Gulisano, M., Pacini, S., Punzi, T., Morucci, G., Quagliata, S., Delfino, G., Sarchielli, E., Marini, M., & Vannelli, G. B. (2009). Cadmium modulates proliferation and differentiation of human neuroblasts. Journal of Neuroscience Research, 87(1), 228-237. https://doi.org/https://doi.org/10.1002/jnr. 21830
- Guo, S., Wu, K., Gao, Y., Liu, L., Zhu, X., Li, X., & Zhang, F. (2018). Efficient removal of Zn (II), Pb (II), and Cd (II) in waste water based on magnetic graphitic carbon nitride materials with enhanced adsorption capacity. Journal of Chemical & Engineering Data, 63(10), 3902–3912.

- Gupta, K., Joshi, P., Gusain, R., & Khatri, O. P. (2021). Recent advances in adsorptive removal of heavy metal and metalloid ions by metal oxide-based nanomaterials. Coordination Chemistry Reviews, 445, 214100. https://doi.org/https://doi.org/10.1016/j.c cr.2021.214100
- Gusain, D., Sahani, S., Sharma, Y. C., & Han, S. S. (2024). Adsorption of cadmium ion from water by using non-toxic iron oxide adsorbent; experimental and statistical modelling analysis. International Journal of Environmental Science and Technology, 1–16.
- Hayat, M. T., Nauman, M., Nazir, N., Ali, S., & Bangash, N. (2019). Environmental Hazards of Cadmium: Past, Present, and Future. Cadmium Toxicity and Tolerance in Plants: From Physiology to Remediation, 163–183. https://doi.org/10.1016/B978-0-12-814864-8.00007-3
- Hosseini, S. M., Alibakhshi, H., Jashni, E., Parvizian, F., Shen, J. N., Taheri, M., Ebrahimi, M., & Rafiei, N. (2020). A novel layer-by-layer heterogeneous cation exchange membrane for heavy metal ions removal from water. Journal of Hazardous Materials, 381, 120884.
- Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L., & Zhang, Q. (2012). Heavy metal removal from water/wastewater by nanosized metal oxides: A review. Journal of Hazardous Materials, 211-212, 317-331. https://doi.org/10.1016/j.jhazmat.2011.1 0.016
- Huang, Q., Chen, Y., Yu, H., Yan, L., Zhang, J., Wang, B., Du, B., & Xing, L. (2018). Magnetic graphene oxide/MgAl-layered double hydroxide nanocomposite: Onepot solvothermal synthesis, adsorption performance and mechanisms for Pb2+, Cd2+, and Cu2+. Chemical Engineering Journal, 341, 1-9. https://doi.org/https://doi.org/10.1016/j.c ej.2018.01.156
- Kim, J. G., Ku, J., Jung, J., Park, Y. S., Choi, G. H., Hwang, S. S., Lee, J.-H., & Lee, A. S. (2024). Ion-exchangeable and sorptive reinforced membranes for efficient electrochemical removal of heavy metal ions in wastewater. Journal of Cleaner Production, 438, 140779.
- Kumar, K. Y., Muralidhara, H. B., Nayaka, Y. A., Balasubramanyam, J., &

## **RESEARCH ARTICLE**

Hanumanthappa, H. (2013). Low-cost synthesis of metal oxide nanoparticles and their application in adsorption of commercial dye and heavy metal ion in aqueous solution. Powder Technology, 246, 125-136. https://doi.org/https://doi.org/10.1016/j.p owtec.2013.05.017

- Lin, J., Su, B., Sun, M., Chen, B., & Chen, Z. (2018). Biosynthesized iron oxide nanoparticles used for optimized removal of cadmium with response surface methodology. Science of The Total Environment, 627, 314-321. https://doi.org/https://doi.org/10.1016/j.s citotenv.2018.01.170
- Liu, J., Ge, X., Ye, X., Wang, G., Zhang, H., Zhou, H., Zhang, Y., & Zhao, H. (2016). 3D graphene/δ-MnO 2 aerogels for highly efficient and reversible removal of heavy metal ions. Journal of Materials Chemistry A, 4(5), 1970-1979.
- Marcano, D. C., Kosynkin, D. V., Berlin, J. M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L. B., Lu, W., & Tour, J. M. (2010). Improved synthesis of graphene oxide. ACS Nano, 4(8), 4806-4814. https://doi.org/10.1021/nn1006368
- Motitswe, M. G., Badmus, K. O., & Khotseng, L. (2024). Application of Reduced Graphene Oxide-Zinc Oxide Nanocomposite in the Removal of Pb(II) and Cd(II) Contaminated Wastewater. In Applied Nano (Vol. 5, Issue 3, pp. 162–189). https://doi.org/10.3390/applnano503001 2
- Ncibi, M. C. (2008). Applicability of some statistical tools to predict optimum adsorption isotherm after linear and nonlinear regression analysis. Journal of Hazardous Materials, 153(1), 207-212. https://doi.org/https://doi.org/10.1016/j.jh azmat.2007.08.038
- Ogata, F., Imai, D., Toda, M., Otani, M., & Kawasaki, N. (2016). Properties of a novel adsorbent produced by calcination of nickel hydroxide and its capability for phosphate ion adsorption. Journal of Industrial and Engineering Chemistry, 34, 172-179.
- Peana, M., Pelucelli, A., Chasapis, C. T., Perlepes, S. P., Bekiari, V., Medici, S., & Zoroddu, M. A. (2023). Biological Effects of Human Exposure to Environmental Cadmium. In Biomolecules (Vol. 13, Issue 1). https://doi.org/10.3390/biom13010036

- Peng, L., Zeng, Q., Tie, B., Lei, M., Yang, J., Luo, S., & Song, Z. (2015). Manganese dioxide nanosheet suspension: a novel absorbent for cadmium (II) contamination in waterbody. Journal of Colloid and Interface Science, 456, 108–115.
- Pohl, A. (2020). Removal of heavy metal ions from water and wastewaters by sulfurcontaining precipitation agents. Water, Air, & Soil Pollution, 231(10), 503.
- Roy, P., Mondal, N. K., & Das, K. (2014). Modeling of the adsorptive removal of arsenic: A statistical approach. Journal of Environmental Chemical Engineering, 2(1), 585-597. https://doi.org/https://doi.org/10.1016/j.je ce.2013.10.014
- Saleem, J., Shahid, U. Bin, Hijab, M., Mackey, H., & McKay, G. (2019). Production and applications of activated carbons as adsorbents from olive stones. Biomass Conversion and Biorefinery, 9(4), 775-802. https://doi.org/10.1007/s13399-019-00473-7
- Şaylan, M., Demirel, R., Ayyıldız, M. F., Chormey, D. S., Çetin, G., & Bakırdere, S. (2022). Nickel hydroxide nanoflower-based dispersive solid-phase extraction of copper from water matrix. Environmental Monitoring and Assessment, 195(1), 133. https://doi.org/10.1007/s10661-022-10653-0
- Sen, T. K., & Sarzali, M. V. (2008). Removal of cadmium metal ion (Cd2+) from its aqueous solution by aluminium oxide (Al2O3): A kinetic and equilibrium study. Chemical Engineering Journal, 142(3), 256-262.
- Sharma, M., Singh, J., Hazra, S., & Basu, S. (2019). Adsorption of heavy metal ions by mesoporous ZnO and TiO2@ZnO monoliths: Adsorption and kinetic studies. Microchemical Journal, 145, 105-112. https://doi.org/https://doi.org/10.1016/j.m

icroc.2018.10.026

- Sreeprasad, T. S., Maliyekkal, S. M., Lisha, K. P., & Pradeep, T. (2011). Reduced graphene oxide-metal/metal oxide composites: Facile synthesis and application in water purification. Journal of Hazardous Materials, 186(1), 921-931. https://doi.org/https://doi.org/10.1016/j.jh azmat.2010.11.100
- Sun, J., Liu, L., & Yang, F. (2020). A WO3/PPy/ACF modified electrode in electrochemical

system for simultaneous removal of heavy metal ion Cu2+ and organic acid. Journal of Hazardous Materials, 394, 122534.

- Suwannahong, K., Wongcharee, S., Kreetachart, T., Sirilamduan, C., Rioyo, J., & Wongphat, A. (2021). Evaluation of the Microsoft Excel Solver Spreadsheet-Based Program for nonlinear expressions of adsorption Isotherm models onto magnetic nanosorbent. Applied Sciences, 11(16), 7432.
- Thy, L. T. M., Thuong, N. H., Tu, T. H., Nam, H. M., Hieu, N. H., & Phong, M. T. (2019). Synthesis of magnetic iron oxide/graphene oxide nanocomposites for removal of cadmium ions from water. Advances in Natural Sciences: Nanoscience and Nanotechnology, 10(2), 25006.
- Vivek, P., Sivakumar, R., Selva Esakki, E., & Deivanayaki, S. (2023). Fabrication of NiO/RGO nanocomposite for enhancing photocatalytic performance through degradation of RhB. Journal of Physics and Chemistry of Solids, 176, 111255. https://doi.org/https://doi.org/10.1016/j.jp cs.2023.111255
- Wan, S., Ding, W., Wang, Y., Wu, J., Gu, Y., & He, F. (2018). Manganese oxide nanoparticles impregnated graphene oxide aggregates for cadmium and copper remediation. Chemical Engineering Journal, 350, 1135–1143.
- Zhang, Y., & Duan, X. (2020). Chemical precipitation of heavy metals from wastewater by using the synthetical magnesium hydroxy carbonate. Water Science and Technology, 81(6), 1130-1136.
- Zheng, Y., Cheng, B., Fan, J., Yu, J., & Ho, W. (2021). Review on nickel-based adsorption materials for Congo red. Journal of Hazardous Materials, 403, 123559.



# Synthesis of Poly(glycerol malonate) Oligomers from Bio-based Sources Utilizing AlCl<sub>3</sub> Catalyst

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**Abstract**: Due to the significant economic and environmental benefits, the demand for biomass-derived building blocks in polymer development has increased in recent years. Bio-based plastics, integral to advancing a circular economy, have consistently been a leading topic among emerging technologies. In this study, we aim to evaluate the effectiveness of different esterification catalysts. To achieve this, we synthesized a range of fully bio-based oligomers using glycerol and malonic acid as starting materials, along with three catalysts: tin(II) 2-ethylhexanoate (stannous octoate, Sn(Oct)<sub>2</sub>), stannous chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O), and aluminum chloride (AlCl<sub>3</sub>). The chemical structures of the synthesized oligomers were confirmed using NMR and FTIR spectroscopy. Thermal properties were assessed using DSC and TGA. FTIR analysis verified successful oligomer synthesis, and a glass transition temperature ( $T_g$ ) of approximately -56 °C was determined via DSC. Additionally, the oligomers exhibited maximum working temperatures at around 278 °C, corresponding to a 50 wt% loss.

**Keywords:** Bio-based oligomers, biopolymers and renewable polymers, polycondensation, catalyst.

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## 1. INTRODUCTION

Despite the advantages polymers offer in terms of energy savings, weight reduction, and durability, their appeal has diminished due to the rapid depletion of petroleum resources and increasing environmental concerns (Iwata, 2015). Bio-based polymers, derived from renewable resources, present a promising alternative to traditional petroleum-based polymers. The demand for biomass-derived building blocks for polymer development has surged in recent years, driven by both economic and environmental considerations. Bio-based plastics have consistently topped the list of emerging technologies, particularly within the framework of a circular economy. Recent research has led to the synthesis of various bio-based polymers, including poly(lactic acid) (PLA) (Balla et al., 2021), poly(glycolic acid) (PGA) (Jem & Tan, 2020), poly(butylene succinate) (PBS) (Wang et al., 2022), cellulosic plastics (Morinval & Averous, 2022), poly(hydroxyalkanoates) (PHA) (Ansari et al., 2021), poly(ε-caprolactone) (PCL) (Acik, 2020), and starch-based plastics (Zhang et al., 2021). These materials have garnered increasing interest from technical and industrial perspectives, with the

potential to replace petroleum-based polymers in diverse applications such as clothing, sanitation, drug delivery, packaging, tissue engineering, agriculture, and toys (Tremblay-Parrado et al., 2021).

Two major challenges in the adoption of bio-based polymers have been their cost and performance. decreased However, costs have due to advancements in bioprocessing technologies and the establishment of global biorefineries that produce bio-based monomers and building blocks (Bozell & Petersen, 2010). For instance, succinic acid, a bio-based monomer, is now commercially produced by companies like BioAmber and Myriant. Over the past two decades, aliphatic polyesters derived from sebacic acid, itaconic acid, 1,4-butanediol, 1,3-propanediol, succinic acid, 2,5furandicarboxylic acid, adipic acid, glycerol, and other compounds have been extensively studied, ranging from rigid plastics to soft elastomers (Fei et al., 2022; Kasmi et al., 2021; Zhang et al., 2021). These materials have attracted significant attention from both academic and industrial sectors. Malonic acid (MA), a dicarboxylic acid derived from glycerol, can function as either a monomer or a crosslinker

(Zhao et al., 2020). While some researchers have explored the use of MA in crosslinking polyvinyl alcohol (PVA) via esterification, its application in polymer synthesis remains relatively underexplored (Qiu & Netravali, 2013). Dogan and Kusefoglu reported some success in polymerizing MA with soybean oil, indicating potential for future studies in this area (Doğan & Küsefoğlu, 2008).

In this study, we aim to evaluate the performance of different esterification catalysts. To this end, we synthesized a variety of fully bio-based oligomers using glycerol and malonic acid as starting materials, in conjunction with three catalysts: AlCl<sub>3</sub>, Sn(Oct)<sub>2</sub>, and SnCl<sub>2</sub>·2H<sub>2</sub>O. AlCl<sub>3</sub>, in particular, is notable for its low environmental impact and costeffectiveness compared to zeolites, transition metal catalysts, and rare earth catalysts. The chemical and thermal properties of the synthesized oligomers were characterized using NMR/FTIR and DSC/TGA techniques.

## 2. EXPERIMENTAL SECTION

## 2.1. Materials

Glycerol (GLY,  $\geq$ 99.5%), malonic acid (MA, 99%), AlCl<sub>3</sub>, Sn(Oct)<sub>2</sub>, stannous chloride dehydrate (SnCl<sub>2</sub>.2H<sub>2</sub>O) and all solvents were purchased from Sigma-Aldrich. All reagents and solvents were used as received without further purification.

## 2.2. Synthesis of PGM Oligomers

Oligomers with various catalysts were produced by a two-step polycondensation method. First stage, esterification, led to the formation of oligomers with only low molecular weight compounds. Then, increasing the temperature and reducing the reaction pressure facilitated the coupling of the oligomer chains by either an esterification or a transesterification reaction. The experiments were run in 100 mL round-bottom flask equipped with a distillation setup and a nitrogen inlet to remove water and other by-products. All reactions of GLY with MA were carried out with a diol /diacid molar ratio of 1.1:1. At the first stage, the reaction mixture was continuously stirred under nitrogen to limit oxidation. The flask was immediately placed into an oil bath at 135 °C and allowed to react for 3 h. After oligomerization, at the second step of polycondensation, the reaction mixture was subsequently heated to final temperature 210 °C. A vacuum of 7 mbar was applied for another 3 h to

remove water vapor. After polymerization, the reaction products were dissolved in chloroform and then precipitated in cold methanol (- 30 °C) to remove the unreacted monomers and catalyst. Precipitated polymer was then filtered and dried in a vacuum oven at room temperature for 24 h.

## 2.3. Characterization

<sup>1</sup>H NMR spectra of oligomers were obtained on a Bruker (Ultrashield Plus Biospin Avance III) 400 MHz NMR spectrometer using tetramethylsilane as the internal standard. CDCl<sub>3</sub> was used as solvent to prepare solutions. The synthesized polymers were characterized by Fourier transform infrared spectroscopy (FTIR) with ATR using a Jasco 6800 at 450-4000 cm<sup>-1</sup> wavelength range with 16 scans. The molecular weights were determined using Agilent 1200 gel permeation chromatograph (GPC). THF was used as eluent, and PMMA standards were used for calibration. The sample concentration was 1 mg/mL and eluent flow rate was 1 mL/min. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed under nitrogen on a Mettler Toledo (DSC 3) and Mettler Toledo (TGA/DSC 3+). For DSC, the samples were heated from room temperature to 160 °C at a rate of 10 °C/min and held for 3 min to eliminate the thermal history. Then, they were cooled to -60 °C and heated again from -60 to 160 °C at a rate of 10 °C/min. For TGA, samples were heated from 25 to 600 °C at 10 °C/min heating rate.

## **3.. RESULTS AND DISCUSSION**

## 3.1. Chemical Structure of Synthesized Oligomers

Various bio-based oligomers were synthesized through a two-step melt polycondensation process using three different catalysts (Figure 1). The initial reactions were carried out at a temperature of 135 °C, selected based on the melting point (135 °C) and boiling point (140 °C) of malonic acid. Following synthesis, the number-average molecular weight  $(M_n)$  of the oligomers ranged from approximately 200 to 400 g/mol, indicating the formation of dimers or oligomers (Table 1). This suggests that the catalysts were not sufficiently effective during the second step, namely, transesterification. Among the catalysts, only the synthesis of PGM using  $\mbox{AlCl}_3$ achieved the desired yield. Therefore, only its characterization was performed, and the results are presented in the following sections.



Figure 1: Image of the PGM oligomer samples produced using AlCl<sub>3</sub>.

Catalyst	M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)	PDI	T₅% (°C)	T <sub>max</sub> (°C)	Residue at 600 °C wt.%	Tg (°C)
AICI <sub>3</sub>	247.7	326.4	1.32	178	268	1.7	-56.5
Sn(Oct) <sub>2</sub>	423.5	434.0	1.02	-	-	-	-
$SnCl_2.2H_2O$	194.9	261.6	1.34	-	-	-	-

 $T_g$  glass transition temperature,  $T_{5\%}$  temperature at 5 % weight loss,  $T_{max}$  temperature at 50 % weight loss.

The chemical structure of the synthesized poly(glycerol malonate) (PGM) oligomers was characterized using <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR analysis revealed that the PGM oligomer backbone consisted of a mixture of alkane and ester bonds (Figure 2). In the <sup>1</sup>H NMR spectrum, the presence of ester bonds was confirmed by the signal at  $\delta = 3.89$  ppm, which corresponds to the COO-

CH<sub>2</sub>- protons from the glycerol repeating units. The chemical shift at  $\delta$  = 3.37 ppm was attributed to the CO-CH<sub>2</sub>-CO- protons from the malonate repeating units. Additionally, the hydroxyl terminal group (HO-CH<sub>2</sub>-) signal was observed at  $\delta$  = 3.71 ppm, consistent with the relatively low molecular weight of the oligomeric samples.



**Figure 2:** <sup>1</sup>H NMR spectrum of the PGM oligomers.

FTIR spectra were taken of the synthesized oligomers to evaluate their chemical composition and are shown in Figure 3. A broad O-H stretching peak can be seen around 3322 cm<sup>-1</sup> indicating the presence of hydroxyl (–OH) from alcohols. Peaks around 2882 cm<sup>-1</sup> correspond to C-H stretching. A

strong absorption peak at approx. 1722 cm<sup>-1</sup> is attributed to C=O stretching vibrations of ester group. Absorption peaks at 1240 and 1044 cm<sup>-1</sup> indicate the presence of C-O stretching and O-CH<sub>2</sub> stretching, respectively.



Figure 3: FTIR spectrum of PGM oligomers with AlCl<sub>3</sub>.

## 3.2. Thermal Properties of Synthesized Oligomers

Differential scanning calorimetry (DSC) was utilized to investigate the thermal properties of the PGM oligomers. The DSC curve for the PGM oligomers synthesized with  $AlCl_3$  is presented in Figure 4, with

the glass transition temperature  $(T_g)$  summarized in Table 1. PGM, being an amorphous oligomer, displayed a glass transition temperature of approximately -56 °C. This low  $T_g$  suggests that PGM could serve as an effective plasticizer, offering advantages in mixing or blending processes.



Figure 4: Second heating DSC curve of PGM oligomers with AlCl<sub>3</sub>.

Thermogravimetric analysis (TGA) was performed on several samples of the synthesized oligomers, with the results summarized in Table 1. The TGA curve for PGM oligomers synthesized with  $AlCl_3$  is shown in Figure 5. TGA analysis allows for the comparison of thermal stability among the samples. Thermal degradation of PGM oligomers occurred in a single degradation step, with an initial decomposition temperature ( $T_{5\%}$ ) of 178 °C. Additionally, the maximum thermal degradation temperature ( $T_{50\%}$ ) was observed at 268 °C. At the end, a small amount of residue (1.71 wt%) was recovered at 600 °C.



Figure 5: TGA curve of PGM oligomers with AlCl<sub>3</sub>.

## 4. CONCLUSION

Bio-based oligomers were successfully synthesized via melt polycondensation using biomonomers glycerol (GLY) and malonic acid (MA), which are industrially produced through fermentation or extraction from biomass. The effects of three esterification catalysts on the chemical and thermal properties of the oligomers were evaluated. Among them, only the synthesis of PGM using AlCl<sub>3</sub> achieved the desired yield. The bio-based oligomers exhibited promising thermal stability, with a  $T_{5\%}$  of 178 °C and a  $T_{50\%}$  of 268 °C when synthesized with AlCl<sub>3</sub>. Given its low cost and minimal environmental impact, AlCl<sub>3</sub> emerged as the most suitable catalyst for the synthesis of these oligomers.

## **5. CONFLICT OF INTEREST**

The authors declare no conflict of interest.

## 6. ACKNOWLEDGMENTS

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## **7. REFERENCES**

- Acik, G. (2020). Bio-based poly (ε-caprolactone) from soybean-oil derived polyol via ringof opening polymerization. Journal Polymers and the Environment, 28(2), 668-675.
- Ansari, S., Sami, N., Yasin, D., Ahmad, N., & Fatma, T. (2021). Biomedical applications of environmental friendly polyhydroxyalkanoates. International Journal of Biological Macromolecules, 183, 549-563.
- Balla, E., Daniilidis, V., Karlioti, G., Kalamas, T., Stefanidou, M., Bikiaris, N. D.,...Bikiaris, D. N. (2021). Poly (lactic Acid): A versatile biobased polymer for the future with multifunctional properties-From monomer synthesis, polymerization techniques and molecular weight increase to PLA applications. *Polymers*, 13(11), 1822.
- Bozell, J. J., & Petersen, G. R. (2010). Technology development for the production of biobased products from biorefinery carbohydratesthe US Department of Energy's "Top 10" revisited. Green Chemistry, 12(4), 539-554.
- Doğan, E., & Küsefoğlu, S. (2008). Synthesis and in situ foaming of biodegradable malonic acid ESO polymers. Journal of Applied Polymer Science, 110(2), 1129-1135.
- Fei, X., Wang, J., Zhang, X., Jia, Z., Jiang, Y., & Liu, X. (2022). Recent progress on bio-based polyesters derived from 2. 5furandicarbonxylic acid (FDCA). Polymers, 14(3), 625.
- Iwata, T. (2015). Biodegradable and Bio-Based Polymers: Future Prospects of Eco-Friendly Plastics. Angewandte Chemie International 3210-3215. Edition, 54(11), https://doi.org/https://doi.org/10.1002/ani e.201410770
- Jem, K. J., & Tan, B. (2020). The development and challenges of poly (lactic acid) and poly (glycolic acid). Advanced Industrial and Engineering Polymer Research, 3(2), 60-70.
- Kasmi, N., Pinel, C., Perez, D. D. S., Dieden, R., & Y. (2021). Synthesis Habibi, and

**RESEARCH ARTICLE** 

characterization of fully biobased polyesters with tunable branched architectures. Polymer Chemistry, 12(7), 991-1001.

- Morinval, A., & Averous, L. (2022). Systems based on thermoplastics: biobased from bioresources to biodegradable packaging applications. Polymer Reviews, 62(4), 653-721.
- Qiu, K., & Netravali, A. N. (2013). Halloysite reinforced biodegradable nanotube nanocomposites using noncrosslinked and malonic acid crosslinked polyvinyl alcohol. Polymer composites, 34(5), 799-809.
- Tremblay-Parrado, K.-K., García-Astrain, C., & Avérous, L. (2021). Click chemistry for the synthesis of biobased polymers and networks derived from vegetable oils. Green Chemistry, 23(12), 4296-4327.
- Wang, G., Hao, X., Dong, Y., Zhang, L., & Sun, R. (2022). Fully bio-based poly (butylene succinate-co-butylene 2, 5thiophenedicarboxylate) with derived from 2, 5-thiophenedicarboxylic acid. Express Polymer Letters, 16(7), 772-784.
- Zhang, Q., Song, M., Xu, Y., Wang, W., Wang, Z., & Zhang, L. (2021). Bio-based polyesters: Recent progress and future prospects. Progress in Polymer Science, 120, 101430.
- Zhao, W., Nolan, B., Bermudez, H., Hsu, S. L., Choudhary, U., & van Walsem, J. (2020). Spectroscopic study of the morphology development of closed-cell polyurethane foam using bio-based malonic acid as chain extender. Polymer, 193, 122344.

Loughlaimi I, Bakher Z, Toukhmi M, Zouhri A. JOTCSB. (2025), 8(1), 47-58. RESEARCH ARTICLE



# Evaluation and Comparative Analysis of Heavy Metal Leaching Efficiency by Nitric Acid, Perchloric Acid and Sulfuric Acid from Moroccan Phosphate Solid Waste

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**Abstract:** This article presents a comprehensive study into the leaching of heavy metals such as AI, As, Cd, Cu, Zn, Ni, Fe and Cr from Moroccan phosphate solid waste. Sulfuric acid, perchloric acid and nitric acid were used as leaching agents at various concentrations (0.5 M, 1 M, 2 M, 3 M and 4 M) under ambient temperature conditions, maintaining a particle size of 160 µm and a stirring time of 1 hour. To optimize the efficiency of metal extraction, research focused on the subtle interplay between acid selection and concentration. Nitric acid appears as the front runner, consistently showing excellent leaching results for all metals, especially at higher concentrations. Although perchloric acid does not exceed the efficiency of nitric acid, its performance is competitive and position it as a viable alternative, with encouraging results, especially at moderate concentrations. Sulfuric acid shows different trends in metal leaching efficiency, highlighting the need for separate and customized approaches. At lower concentrations it shows moderate effectiveness, with leaching efficiency varying depending on the metal. As acid concentration increases, extraction efficiency changes, requiring careful consideration of specific metal properties. In the hierarchy of leaching agents, the position studied is nitric acid, compared to sulfuric acid during metal leaching.

**Keywords:** Leaching process, heavy metal, nitric acid, perchloric acid, sulfuric acid, Moroccan phosphate solid waste, comparative analysis.

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## 1. INTRODUCTION

Heavy metal pollution is one of the major environmental problems today. Most heavy metal ions are toxic to living organisms. Heavy metals are present in nature and industrial waste. The main source of heavy metal pollution is metal plating, mining, smelting, battery manufacturing, tanneries, petroleum refining, pigment manufacturing, etc. (Sulaymon et al., 2014; Yuntao Chen et al., 2024). Heavy metals are defined as metals with a specific density of greater than 5 g/cm<sup>3</sup>, this definition includes the alkali metals, alkaline earth metals, lanthanides and actinides, which are not considered heavy elements in a chemical sense, while excluding some other elements such as arsenic, due to its chemical and ecological effects, it is often considered a heavy metal. One classification that can combine these properties and explain the similarities in mechanisms of heavy metal toxicity in different organisms is based on equilibrium constants describing the formation of metal ion ligand complexes.

Therefore, there are three classes of metals with different bonding preferences. Elements with an affinity for oxygen containing ligands belong to class A, elements with an affinity for nitrogen- or sulfur-containing ligands belong to class B, and elements with intermediate characteristics have an affinity for O<sup>-</sup>, S<sup>-</sup> or N<sup>-</sup> containing ligands belonging to borderline (Stanković et al., 2018).

Based on coordination chemistry and the effects on the environment, heavy metals are all in the class B and the borderline group (Stanković et al., 2018; Kumar Sharma et al., 2004).

The principal elements classified as heavy metals include Cr, Mn, Co, Cu, Zn, Mo, Hg, Ni, Sn, Pb, Cd, Sb, etc. (Sulaymon et al., 2014).

Cd with an atomic number of 48 and an atomic weight of 112.41, is classified within group XII of the periodic table of chemical elements. It occurs at trace concentrations, naturally associated with sulfide ores of zinc, lead and copper. Human activities including the combustion of fossil fuels and the release of leachate from landfill sites, agricultural areas and mining waste, particularly those linked to zinc and lead mining significantly to operations, contribute the contamination of the environment with cadmium (Genchi et al., 2020).

Cr is the seventh most abundant element in the earth. With an atomic number of 24 and a mass number of 52, it occupies a place in group 6 and period 4 of the periodic table. It exhibits various oxidation states, ranging from 0 to +6, with the most stable states being 0, +3 and +6. The primary source of chromium is chromite ore, where it predominantly exists in the +3 oxidation state. However, industrial processes produce hexavalent chromium and the elemental form of the metal (Mukherjee et al., 2013).

Cu is a transition metal, found in nature in two oxidation states: Cu (I) and Cu (II). Cu (I) is a soft and durable metal while Cu (II) is borderline according to the hard and soft acids and bases classification (Dupont et al., 2011). The mainly source of environmental contamination due to printed including copper mining, circuits, metallurgical, fiber production, pipe corrosion and metal plating industries. Additionally, other significant sectors releasing copper into their effluents including the paper and pulp, petroleum refining and wood preserving industries (Sulaymon et al., 2014).

Ni is the 24<sup>th</sup> most abundant element in the earth. With an atomic number of 28 and an atomic weight of 58.71. It is typically found in igneous rocks, either in its elemental form or in conjunction with iron (Amari et al., 2017). Nickel is naturally released into the environment through processes such as windblown, weathering of rocks and wildfires. Human made activities, including the operations of foundries and battery manufacturing plants, also contribute to the environmental release of nickel. Additionally, nickel can be discharged into the environment through sources like tobacco use and the use of stainless-steel kitchenware (Kiran et al., 2021).

As is classified as a metalloid, is naturally present on earth, being the 20<sup>th</sup> most abundant element. It is a constituent of over 245 different minerals. The inorganic form, mainly consisting of arsenic and arsenate compounds, poses a health hazard to humans (Guha Mazumder, 2008). Arsenic is a common occurrence in nonferrous ores such as copper, lead, zinc, gold and uranium. As is a predominant component in specific ores, such as the copper mineral enargite, while it exists as a trace impurity in other ore types. Unregulated human activities such as smelting metal ores, using arsenic based pesticides, and using wood preservatives, can also lead to direct releases of arsenic into the environment (Choong et al., 2007).

As base metal prices have increased significantly in recent years, the extraction of these metals from various waste sources, including solid phosphate waste, has become increasingly important (Huang et al., 2011).

Ongoing global efforts include in depth research aimed at identifying efficient and cost-effective ways to process solid waste and extract valuable metals from it (Ajiboye et al., 2019).

In practice, innovative hydrometallurgical methods for metal extraction have emerged, including hydrothermal techniques (Zhang et al., 2006), subcritical water treatment (Zhang et al., 2006), and fungal bioleaching (Ishigaki et al., 2005). Although those methods have promising extraction capabilities, they often increase operating costs or extend leaching times. Therefore, it is recommended to give priority to performing the process at ambient leaching temperature, emphasizing the importance of careful selection of suitable leaching agents to achieve satisfactory treatment efficiency throughout the process (Huang et al., 2011).

Leaching is a technique for dissolving soluble substances from a mixture of insoluble solids. The solvent used in the leaching process is called a leaching agent (Yuliusman et al., 2018), and various leaching agents, such as inorganic acids such as sulfuric acid, hydrochloric acid and nitric acid (Hussaini et al., 2021), and organic acids (Fatima et al., 2024) such as citric acid (Wu et al., 2006), oxalic acid (Nugteren et al., 2001; Fengyuan et al., 2024), acetic acid (Fuoco et al., 2005), tartaric acid (Smichowski et al., 1998), and chelating agents such as nitrilotriacetic acid (NTA) (Wu et al., 2022), ethylenediaminetetraacetic acid (EDTA) (Opi et al., 1999) and diethylenetriaminepentaacetic acid (DTPA) (Singh et al., 2013), and in some cases alkaline solutions such as ammonium hydroxide and sodium hydroxide (Ntumba Malenga et al., 2015), can be used to extract heavy metals. Of the above-mentioned leaching agents, sulfuric acid and hydrochloric acid generally appear to be the most suitable (Huang et al., 2011; Shokrullah et al., 2024).

The experimental approach was to perform a leaching process of solid phosphate waste using different acid treatments, each with a specific concentration. Sulfuric acid, nitric acid and perchloric acid were selected as the main agents for metal extraction. The entire process was performed at ambient temperature. The purpose of this study was to determine the different effects on the efficiency of extraction of Fe, Al, Cd, Ni, Zn, Cr, As and Cu from waste materials by varying the concentration of these acids. Comparative analysis of these acid treatments provides valuable insights into optimal conditions for metal recovery from

Moroccan phosphate solid waste under ambient temperature conditions.

## 2. EXPERIMENTAL STUDIES

## 2.1. Materials And Reagents

The samples used for the leaching process in this study obtained from the Moroccan phosphate solid waste, we utilized a series of chemical reagents, including sulfuric acid, nitric acid and perchloric acid with different concentration (0.5 M to 4 M).

In our study of Moroccan phosphate solid waste, we used a variety of materials and techniques to analyze and characterize the samples. The GFL 3040 jar test from Gesellschaft Für Labortec Overhead Shakers; was used to stir the samples; to ensure efficient mixing and dispersion during the leaching process. This step is critical to achieve optimal leaching efficiency.

Product	Chemical formula	CAS number	Analysis method	Purity (conductivity and pH of water)
Sulfuric acid	$H_2SO_4$	7664-93-9		95%
Perchloric acid	HCIO <sub>4</sub>	7601-90-3	VT <sup>1</sup>	70%
Nitric acid	HNO₃	7697-37-2		69%
Distilled water	H <sub>2</sub> O	7732-18-5	CA <sup>2</sup>	Conductivity: 21.4 µS/cm pH: 7.61

#### **Table 1**: Product utilization descriptions.

1: Volumetric titration,	, 2: Conductimetric analy	/sis
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To measure the ion concentration after the leaching process, we used inductively coupled plasma (ICP) analysis. ICP allows to accurately quantify the concentrations of different ions in solution, and gain important insights into the leaching efficiency and distribution of elements in solid waste samples. Moreover, ICP was also instrumental in the analysis of metal ion concentrations within the solid waste, further enhancing our understanding of the waste's elemental composition.

Furthermore, for detailed analysis of a solid waste samples' crystalline structure and composition, we used X-ray diffraction (XRD). This technique uses diffraction patterns of X-ray to identify the crystal structure and composition of the samples providing valuable information about the chemical compounds present in the solid waste. X-ray diffraction analysis was conducted on all solid samples to assess the composition of solid phases within diverse saturated solutions. This analytical process was carried out using a BRUKER D2 phase shifter instrument equipped with a LYNXEYE detector, utilizing a Cu-Ka wavelength of 1.541874 Å. Each stable solid underwent analysis within a temperature range spanning from 10 to 80 °C for a allowing duration of 20 minutes, for а comprehensive characterization of the solid phases present.

## 2.2. Experimental Methodology

In a 250 mL flask, a precisely measured 10 grams of the solid waste sample were added. Subsequently, different concentrations of the previously prepared acid solutions were introduced into the flask, with concentrations ranging from 0.5 M to 4 M. These acids served as the leaching agents and were carefully selected to optimize the leaching process.

The entire setup was maintained at a constant temperature of 24°C throughout the experiments to ensure uniform conditions during the leaching process. The mixture is stirred continuously for one hour to ensure effective contact between the solid waste and the leaching agent.

After the stirring period, the samples were allowed to stand to facilitate the separation of solid and liquid phases. The decanted liquid was then filtered through a 0.45  $\mu$ m filter to remove any remaining solid residue. This filtration process ensured that only the liquid phase without solid particles remained for later analysis.

The leachate obtained was analyzed using ICP for a comprehensive evaluation of the chemical composition, especially the concentration of various ions and metals. This analytical technique enabled accurate quantification of dissolved ions and provided valuable insight into leaching efficiency and liquid phase composition resulting from the interaction of solid waste with different concentrations of leaching acid.

# 2.3. Characterization Of Phosphate Solid Waste

#### 2.3.1. Preparation of samples

Before further analysis, the solid waste samples underwent a careful pretreatment process to ensure suitability for subsequent experiments. The first step was to dry the samples in an oven set at 135°C for 30 min to 1 h. This controlled drying helped remove interparticle moisture, an important step to prevent clogging that may occur during the subsequent grinding process.

The samples were milled using a rotating disc mill consisting of a fixed steel disc and a movable counterpart. This grinding process reduces the sample to a fine consistency, typically reaching a

## 2.3.2. ICP characterization

fineness of around 160  $\mu m.$  The purpose of this grinding process was to completely homogenize the sample.

After the grinding process, the obtained material was sieved through 160  $\mu$ m sieve. The material that did not pass the sieve was manually ground using a mortar and pestle and mixed with the material that passed the sieve.

To make certain the entire elimination of any ultimate moisture, the homogenized pattern underwent a very last drying step. It turned located in an oven set at a decrease temperature, commonly 105°C, for a length of hours, taking into account the full removal of residual humidity. This complete pattern guidance ensured that the solid waste was in an optimal state for subsequent analytical procedures and minimized the capacity for moisture associated interference.

Table 2: Analysis of the utilized phosphate solid waste in this study.

Elements	Units	Values for
Mg	%	14.2
Fe	%	8.2
Al	%	15.2
Cd	Ppm	418
Ni	%	50.96
Zn	%	426.4
Cr	%	229.8
As	%	10.96
Cu	%	50.59

Table 3: Operation conditions for ICP.

Parameters		Units	Values
Rf power (w)		w	1300.0
Plasma Ar flow (L/	min)	L/min	12.0
Auxiliary Ar flow (	L/min)	L/min	0.2
Nebulizer Ar flow	(L/min)	L/min	0.7
Delay time (s)		S	40.0
Measurement	Axial	-	All
mode:			
	Radial	-	Iron,
			Aluminum, CaO

## 2.3.3. Solid waste characterization

X-ray diffraction (XRD) analysis of our solid phosphate waste samples (Figure 1) revealed the presence of several significant crystalline compounds. The most prominent diffraction peaks in the spectrum correspond to several different minerals such as Mg<sub>3</sub>AlSi<sub>3</sub>O<sub>12</sub>I<sub>12</sub>,  $As_8Cu_{12}S_{18}$ ,  $Mg_4FeCa_4Si_4O_{16}$ ,  $Zr_4Cr_4NiCuO_{14}$  and  $CdMg_5C_6O_{18}$ . Each peak in the XRD spectrum is closely related to а specific interplanar distance and corresponding 20 diffraction angle, forming a unique signature for each compound. The relative intensities of these peaks provide valuable insight into the abundance of each mineral in the sample.

The presence of this compound is confirmed by the distinct peaks observed in the diffraction pattern. This XRD analysis provides a comprehensive understanding of the mineral composition of the samples which is essential for further studies. Our results provide a solid foundation for a detailed study of the chemical leaching processes involved in the removal of elements such as Mg, Cd, Fe, Al, Ni, Zn, Cr and As from samples.



Figure 1: X-ray diffraction pattern of phosphate solid waste sample.

**Table 4:** Elemental analysis references, content of pattern from X-pert Highscore.

Ref. Code	Score	Compound Name	Scale	Chemical Formula
			Factor	
96-150-9454	20	Ag (Mg <sub>0.5</sub> Zn <sub>0.5</sub> )	0.054	Mg <sub>0.50</sub> Zn <sub>0.50</sub> Ag <sub>1.00</sub>
96-901-0226	12	Magnesite	0.178	$Cd_{0.60} Mg_{5.40} C_{6.00} O_{18.00}$
96-900-0637	11	Monticellite	0.134	Mg <sub>3.72</sub> Fe <sub>0.28</sub> Ca <sub>4.00</sub> Si <sub>4.00</sub> O <sub>16.00</sub>
96-900-2230	0	Clinochlore	11.732	Mg <sub>2.97</sub> Al <sub>0.99</sub> Si <sub>3.04</sub> O <sub>12.00</sub> I <sub>12.00</sub>
96-900-0465	14	Sinnerite	0.348	As <sub>8.00</sub> Cu <sub>12.00</sub> S <sub>18.00</sub>
96-100-8717	12	Zirconium	0.061	Zr <sub>4.00</sub> Cr <sub>4.80</sub> Ni <sub>1.60</sub> Cu <sub>1.60</sub> D <sub>14.04</sub>
		chromium copper		
		nickel deuteride		

## 3. RESULTS AND DISCUSSION

## 3.1. Leaching Metals With Sulfuric Acid

In our experimental study, we examined the interaction between sulfuric acid concentration H<sub>2</sub>SO<sub>4</sub> (M) and aluminum concentration dissolved (%). As shown in Figure 2 if we gradually increase the H<sub>2</sub>SO<sub>4</sub> concentration, we observed a steady decrease in the aluminum content in the solution. At an initial H<sub>2</sub>SO<sub>4</sub> concentration of 0,5M, the Al extraction rate was relatively high. However, as the acid concentration increases, the AI content shows a significant decrease. When the acid reaches 4 M, the Al concentration has dropped significantly to only 0.484%. This downward indicates that sulfuric acid is effective in extracting aluminum. evidenced by the as inverse relationship between acid concentration and Al concentration. Our results are consistent with previous studies in this area, which have consistently shown that increasing the molar concentration of sulfuric acid results in a decrease in the aluminum content in the solution. This phenomenon is well documented in studies of the leaching of aluminum and other metals from various matrices. For example, Wang P et al (Wang P et al., 2021) in their study of extraction of aluminum from Coal Fly Ash observed further increase in H<sub>2</sub>SO<sub>4</sub> concentration did not result in significant or substantial increases in Al extraction.

As shown in the Figure 3, at an initial sulfuric acid concentration of 0.5 M, the chromium concentration was 201.9%. However, when the sulfuric acid concentration was increased to 1 M, the value increased significantly to 476.4%. This increase was not consistent, as at 2 M of sulfuric acid, the chromium concentration reached 1041%, indicating a significant increase. However, when we switched to 3 M the chromium concentration dropped to 319.8%. This decrease continued with 4 M.

These results highlight the sensitivity of the chromium leaching process to sulfuric acid concentration. They highlighted а critical optimization point where a specific concentration of sulfuric acid promotes the maximum chromium extraction. Beyond this point, higher acid concentrations do not necessarily result in more efficient chromium extraction. Previous studies in this field have revealed a complex relationship between acid concentration and chromium leaching efficiency. Our results are consistent with this established knowledge in several aspects. Notably, increasing the sulfuric acid concentration did not improve the chromium concentration in solution, a trend that mirrors observations in previous studies (Silva J et al., 2005).



Figure 2: Effect of sulfuric acid concentration on the extraction of Al from phosphate solid waste.



**Figure 3:** Effect of sulfuric acid concentration on the extraction of Cr from phosphate solid waste.

Figure 4 shows the impact of varying sulfuric acid concentration on the leaching efficiency of Cu from our solid phosphate waste sample. The initial acid concentration significantly increase in the amount of copper extracted. increased acid However, at higher concentrations, a copper leaching efficiency decrease in was observed, and leaching finally stopped at 3 M and 4 M sulfuric acid. This observation highlights the dynamic relationship between sulfuric acid concentration and copper leaching efficiency. Our results initially support the assumption that low to moderate acid concentrations promote copper highlight an important extraction, but also threshold. At some point (shown here at 2 M H<sub>2</sub>SO<sub>4</sub>), increasing the acid concentration does not proportionally improve copper leaching. The subsequent complete cessation of leaching at 3 M and 4 M highlights the importance of precise control of acid concentration to optimize copper recovery while minimizing waste. Although our results support previous studies such as those by Zhang Y et al (2019), who emphasized the improvement of copper extraction with increasing acid concentration, they also highlighted the importance of the optimal range of acid concentration. Beyond this range, further increases provide no additional benefit.



**Figure 4:** Effect of sulfuric acid concentration on the extraction of Cu from phosphate solid waste.

Building on our investigation of the effect of sulfuric acid on metal leaching efficiency, we shifted our focus to leaching of As, another important element presents in solid phosphate waste samples. As shown in Figure 5 at an initial  $H_2SO_4$  concentration of 0.5 M, the arsenic concentration is determined to be 4.089%. As the acid concentration was gradually increased, the amount of arsenic leached continued to increase. This increase persisted at 2 M. However, a significant change was observed at 3 M as the arsenic concentration decreased significantly to 1.791%. This reduction in leached arsenic continues at 4M. The results indicate a critical point, around 3 M of  $H_2SO_4$ , where continued increases in acid concentration do not result in a proportional increase in leached arsenic concentration.



**Figure 5:** Effect of sulfuric acid concentration on the extraction of As from phosphate solid waste.

As can be seen from Figure 6, there is a significant trend in cadmium leaching efficiency as the sulfuric acid concentration changes. The initial increase in acid concentration increased the amount of cadmium extracted. However, as the acid concentration continued to increase, a decrease in yield was observed, highlighting the existence of an optimal acid concentration range for efficient cadmium recovery. These results confirm the findings obtained by Safarzadeh et al (Safarzadeh et al., 2009).



Figure 6: Effect of sulfuric acid concentration on the extraction of Cd from phosphate solid waste.

In conclusion, based on all these results, we studied the leaching process of several elements, namely Al, Cr, As, Cu and Cd, using different concentrations of sulfuric acid H<sub>2</sub>SO<sub>4</sub>. Our results show significant trends for each element. For aluminum, we observed a gradual decrease in concentration with increasing H<sub>2</sub>SO<sub>4</sub> concentration, highlighting the importance of acid optimization. The concentration of chromium Cr increases up to a certain point, and then decreases again, indicating that there is an optimal range. As exhibits a similar reaction to chromium, with significantly lower concentrations at higher acid levels. In contrast, the Cu concentration increased with increasing H<sub>2</sub>SO<sub>4</sub> concentration, which is consistent with the trend observed in other studies. Finally, the concentration of Cd initially increases and then gradually decreases at higher acid levels. These results highlight the importance of precise control of sulfuric acid concentration during the leaching process of these elements, especially for optimizing their recovery and waste reduction.

# 3.2. Leaching Metals with Perchloric Acid and Nitric Acid

Experimental results (Figure 7) on leaching aluminum varying concentrations of nitric acid and perchloric acid provided valuable insights into the leaching efficiency of these two acids. Remarkably, the results show a marked contrast in their performance. Nitric acid shows significant advantages in the extracting aluminum especially as the acid concentration increases. At a low concentration of 0.5 Μ. the aluminum concentration extracted with nitric acid was only 0.039%, indicating limited effectiveness under mild conditions. However, when the nitric acid concentration increased to 1 M, the aluminum extraction efficiency increased significantly to 4.241%, indicating a significant improvement in leaching performance. This trend continues as the concentration continues to increase. In contrast, the efficiency of perchloric acid in extracting aluminum was relatively low, and at most concentrations, the extraction rate is significantly lower than that of nitric acid. Even at 2 M concentration, where nitric acid shows significant efficiency, perchloric acid can only achieve a concentration of 4.434%. As the concentration increases, the difference between the two acids becomes more pronounced, with perchloric acid concentration 4 M reaching 3.966%.

The trend of higher aluminum extraction efficiency with increasing nitric acid concentration is consistent with the literature. The study by Pepper R et al (2016) showed that higher concentrations of nitric acid led to an increased aluminum dissolution, which is consistent with our experimental results. Compared to nitric acid, perchloric acid is used less frequently in aluminum leaching, and its efficiency tends to be less.





As shown in the Figure (8), the results of As leaching experiments using varying concentrations of nitric acid and perchloric acid provide valuable insights into the efficiency of these acids in arsenic extraction. Nitric acid shows clear advantages in extraction, especially as arsenic the acid concentration increases. At a low concentration of 0.5 M only a small amount of arsenic was extracted with nitric acid. However, as the nitric acid concentration increases to 1 M, the extraction rate of arsenic increases significantly, reaching a

concentration of 4.978%. This increase continues as the concentration continues to rise. In contrast, perchloric acid showed limited arsenic leaching efficiency at lower concentrations, with negligible arsenic extraction at 0,5 M. At a concentration of 1 M, a small amount of arsenic was extracted. However, at higher concentrations, the arsenic extraction yield by perchloric acid improved. Despite this improvement, the efficiency of perchloric acid has always lagged behind that of nitric acid.

Compared with previous studies by Ling H et al (2022), our study showed a similar trend in increasing arsenic concentration with increasing nitric acid concentration. Notably, Ling H et al achieved these results while conducting experiments at a higher temperature of 60°C, which requires the expenditure of energy. In contrast, our study has a clear advantage because it achieves equivalent arsenic extraction efficiency without increasing the temperature. This represents a potentially more energy efficient and practical method for arsenic leaching. Our approach is not only consistent with existing literature, but also introduces an innovative aspect that reduces reliance on high temperatures, thereby providing potential cost and sustainability benefits.



Figure 8: Effect of nitric acid and perchloric acid concentration in the extraction of As from phosphate solid waste.

For Cd, Figure 9 shows that nitric acid is an efficient leaching agent, especially as the acid concentration increases. This trend is consistent with previous research conducted by Saleh M et al (2021) (32). At a low concentration of 0.5 M, no cadmium was extracted. However, as the nitric acid concentration increased to 1 M, the cadmium extraction yield increased significantly to 10.95 ppm, highlighting the improvement in leaching performance. This trend continues to increase. On the other hand, perchloric acid showed relatively cadmium leaching low efficiency at low concentrations and extraction results were

moderate. However, as the perchloric acid concentration increased, an improvement in cadmium extraction was observed. It is important to note that the effectiveness of perchloric acid still lower than that obtained with nitric acid at higher concentrations.



**Figure 9:** Effect of nitric acid and perchloric acid concentration in the extraction of Cadmium from phosphate solid waste.

As we can see in Figure 10, for Fe leaching, nitric acid exhibited a limited efficiency in extraction, as evidenced by the low extraction yield at different concentrations. The lack of significant iron extraction at a concentration of 0.5 M is consistent with the difficult nature of iron leaching, especially in the presence of nitric acid. The small amount of iron extracted, even at higher concentrations, suggests that nitric acid may not be the ideal choice for iron leaching in this context.

In contrast, perchloric acid exhibited slightly improved iron separation efficiency, especially at higher concentrations. The extraction efficiency with perchloric acid was significantly better than that obtained with nitric acid.



Figure 10: Effect of nitric acid and perchloric acid concentration in the extraction of iron from phosphate solid waste.

For Ni leaching results (Figure 11) show that both nitric acid and perchloric acid are effective agents extraction, for nickel each with distinct effectiveness trends. Nitric acid has significant ability to dissolve nickel, and this efficiency increases with increasing acid concentration. At a concentration of 1 M, the nickel extraction yield increased significantly to 125.6%, highlighting the effectiveness of nitric acid leaching nickel from samples. The trend continues to improve and reaches a pick at a concentration of 3 M. These results highlight the suitability of nitric acid for leaching, especially hiaher nickel at acid concentration, without the need for additional factors such as high temperatures. On the other hand, perchloric acid also proved to be an effective nickel leaching agent, with high leaching efficiency observed at concentrations 2 M and 3 M. Significant extraction yields of 128.2% and 121.4% concentrations, were obtained at these respectively, highlighting the effectiveness of nickel perchlorate leaching in this specific experimental setting. These results indicate that perchloric acid, especially at the concentrations mentioned above, can be a valuable alternative for nickel extraction and provide flexibility in the leaching process.



Figure 11: Effect of nitric acid and perchloric acid concentration in the extraction of Ni from phosphate solid waste.

As shown in Figure 12, Zn leaching experiment results showed that nitric acid could effectively leach zinc at a lower concentration, when the concentration is 1 M, the extraction rate is significantly reaching 394.9%. However, it is worth noting that the zinc extraction efficiency decreases with increasing nitric acid concentration, as shown by the decreasing concentrations of 2 M, 3 M and 4 M. This pattern suggests that moderate concentrations of nitric acid may be most effective for zinc leaching. In contrast, perchloric acid showed relatively stable and higher efficiency in zinc extraction, especially at higher concentrations (2 M, 3 M and 4 M). The extraction yields remained very constant. This suggests that perchloric acid may be a suitable choice for zinc leaching, especially when higher concentrations are required.



Figure 12: Effect of nitric acid and perchloric acid concentration in the extraction of Zinc from phosphate solid waste.

## 3.3. Comparison Between Different Acids

A comprehensive comparison of the leaching of cadmium Cd, aluminum Al and arsenic As from solid phosphate waste using sulfuric acid, nitric acid and perchloric acid revealed complex patterns. For cadmium leaching (Figure 13 (a)), sulfuric acid consistently showed relatively low efficiency at all concentrations, while nitric acid showed a significant increase in efficiency, peaking at concentration 2, and perchloric acid showed competitive efficiency at the same concentration. In aluminum leaching (Figure 13 (b)), nitric acid has proven to be the most effective leaching agent, with the leaching efficiency increasing significantly as the concentration increases, while perchloric acid maintains a relatively stable leaching rate. However, as the concentration increases, the effectiveness of sulfuric acid gradually decreases. For the leaching of arsenic (Figure 13 (c)), sulfuric acid showed constant efficiency at concentration 1 M, while nitric acid showed a significant increase and reached a maximum at concentration 3 M, and perchloric acid showed efficient extraction, especially at concentration 2 M. The different trends between the three elements emphasize the different interactions of acid selection and concentration in optimizing the leaching process. Nitric acid is consistently an effective leaching agent, while perchloric acid is competitively efficient.





Figure 13: Comparison of the extraction efficiency of Cadmium (a), Aluminum (b) and Arsenic (c) with nitric acid, sulfuric acid and perchloric acid.

## 3. CONCLUSION

Recovering metals from solid phosphate waste multifaceted challenges, presents and the selection of a suitable leachate plays a vital role in effective recovery. In this study, the effectiveness of sulfuric acid, nitric acid and perchloric acid in dissolving Al, Cd, As, Cu, Cr, Fe, Ni and Zn in waste samples was examined. An important aspect of this study was to perform experiments at ambient temperature conditions, consciously varying acid concentrations (0.5 M, 1 M, 2 M, 3 M and 4 M). Additionally, the particle size of the samples was standardized to 160 µm to ensure uniform leaching. The stirring time was maintained at one hour, which helped control the experimental conditions.

Nitric acid has consistently proven to be an effective leaching agent, with significantly improved efficiency for all elements, especially at higher concentrations. Although perchloric acid is not more efficient than nitric acid, its performance is competitive and positions it as a viable alternative. Sulfuric acid, on the other hand, showed a different trend, highlighting the importance of developing a customized approach based on the specific properties of the element.

In summary, this study provides valuable insights into the optimized use of sulfuric acid, nitric acid and perchloric acid for the extraction of metals from solid phosphate waste. The findings not only expand our understanding of leaching kinetics but also provide solid foundation for the а development of sustainable and efficient extraction methods. These findings are expected to impact waste management practices and provide potential solutions to the challenges posed by metal leaching from complex waste matrices.

### 4. CONFLICT OF INTEREST

The authors have no conflicts of interest to declare.

#### 5. ACKNOWLEDGMENTS

Not applicable.

#### **6. REFERENCES**

Ajiboye, E. A., Panda, P. K., Adebayo, A. O., Ajayi, O. O., Tripathy, B. C., Ghosh, M. K., & Basu, S. (2019). Leaching kinetics of Cu, Ni and Zn from waste silica rich integrated circuits using mild nitric acid. *Hydrometallurgy*, 188, 161–168. https://doi.org/10.1016/j.hydromet.2019.06. 016

- Amari, T., Ghnaya, T., & Abdelly, C. (2017). Nickel, cadmium and lead phytotoxicity and potential of halophytic plants in heavy metal extraction. In *South African Journal of Botany* (Vol. 111, pp. 99–110). Elsevier B.V. https://doi.org/10.1016/j.sajb.2017.03.011
- Chen, Y., Wang, J., Gao, Z., Cui, M., & Huang, R. (2024). Preparation and Application of Stabilizing Agents for Solidification of Heavy Metal-Contaminated Soil under Low-Temperature Conditions. *ChemEngineering*, 8(5), 89. <u>https://doi.org/10.3390/chemengineering805</u> 0089
- Choong, T. S. Y., Chuah, T. G., Robiah, Y., Koay, F. L. G., & Azni, I. (2007). Arsenic toxicity, health hazards and removal techniques from water: an overview. In *Desalination* (Vol. 217). http://www.epa.gov/
- Dupont, C. L., Grass, G., & Rensing, C. (2011). Copper toxicity and the origin of bacterial resistance - New insights and applications. In *Metallomics* (Vol. 3, Issue 11, pp. 1109– 1118). https://doi.org/10.1039/c1mt00107h
- Fatima, S., Khosa, M. K., Noor, A., Qayyum, S., & el Oirdi, M. (2024). Hydrometallurgical Extraction of Valuable Metals by Mixed Acid Leaching System for Used Lithium-Ion Batteries. Sustainability (Switzerland), 16(16). https://doi.org/10.3390/su16166817
- Fuoco, R., Ceccarini, A., Tassone, P., Wei, Y., Brongo, A., & Francesconi, S. (2005). Innovative stabilization/solidification processes of fly ash from an incinerator plant of urban solid waste. *Microchemical Journal*, 79(1–2), 29–35. <u>https://doi.org/10.1016/j.microc.2004.10.011</u>
- Genchi, G., Sinicropi, M. S., Lauria, G., Carocci, A., & Catalano, A. (2020). The effects of cadmium toxicity. In International Journal of Environmental Research and Public Health (Vol. 17, Issue 11). MDPI AG. <u>https://doi.org/10.3390/ijerph17113782</u>
- Guha Mazumder. (2008). Chronic arsenic toxicity & human health. <u>http://journals.lww.com/ijmr</u>
- Huang, K., Inoue, K., Harada, H., Kawakita, H., & Ohto, K. (2011). Leaching of heavy metals by citric acid from fly ash generated in municipal waste incineration plants. *Journal* of Material Cycles and Waste Management, 13(2), 118-126. https://doi.org/10.1007/s10163-011-0001-5

- Hussaini, S., Kursunoglu, S., Top, S., Ichlas, Z. T., & Kaya, M. (2021). Testing of 17-different leaching agents for the recovery of zinc from a carbonate-type Pb-Zn ore flotation tailing. *Minerals Engineering*, *168*. <u>https://doi.org/10.1016/j.mineng.2021.10693</u> 5
- Hussaini, S., Tita, A. M., Kursunoglu, S., Kaya, M., & Chu, P. (2024). Leaching of Nickel and Cobalt from a Mixed Nickel-Cobalt Hydroxide Precipitate Using Organic Acids. *Minerals*, 14(3). <u>https://doi.org/10.3390/min14030314</u>
- Ishigaki, T., Nakanishi, A., Tateda, M., Ike, M., & Fujita, M. (2005). Bioleaching of metal from municipal waste incineration fly ash using a mixed culture of sulfur-oxidizing and ironoxidizing bacteria. *Chemosphere*, 60(8), 1087–1094. https://doi.org/10.1016/j.chemosphere.2004. 12.060
- Kiran, Bharti, R., & Sharma, R. (2021). Effect of heavy metals: An overview. *Materials Today: Proceedings*, *51*, 880–885. https://doi.org/10.1016/j.matpr.2021.06.278
- Kumar Sharma, R., & Agrawal, M. (2004). Biological effects of heavy metals: An overview. Journal of Environmental Biology. <u>http://www.geocities.com/Lenviron\_biol/J.Env</u> <u>iron.Biol.26</u>
- Ling, H., Malfliet, A., Blanpain, B., & Guo, M. (2022). Selective removal of arsenic from crude antimony trioxide by leaching with nitric acid. *Separation and Purification Technology*, 281. <u>https://doi.org/10.1016/j.seppur.2021.11997</u> <u>6</u>
- Mukherjee, K., Saha, R., Ghosh, A., & Saha, B. (2013). Chromium removal technologies. *Research on Chemical Intermediates*, 39(6), 2267–2286. <u>https://doi.org/10.1007/s11164-012-0779-3</u>
- Ntumba Malenga, E., Mulaba-Bafubiandi, A. F., & Nheta, W. (2015). Alkaline leaching of nickel bearing ammonium jarosite precipitate using KOH, NaOH and NH4OH in the presence of EDTA and Na2S. *Hydrometallurgy*, *155*, 69– 78. <u>https://doi.org/10.1016/j.hydromet.2015.04.</u> 004
- Nugteren, H. W., Janssen-Jurkovícová, M., & Scarlett, B. (2001). Improvement of Environmental Quality of Coal Fly Ash by Applying Forced Leaching. http://www.flyash.info

Loughlaimi I, Bakher Z, Toukhmi M, Zouhri A. JOTCSB. (2025), 8(1), 47-58. RESEARCH ARTICLE

- Opi, N. P., Tambouris, S., & Kontopoulos, A. (1999). REMOVAL OF HEAVY METALS FROM CALCAREOUS CONTAMINATED SOILS BY EDTA LEACHING.
- Pepper, R. A., Couperthwaite, S. J., & Millar, G. J. (2016). Comprehensive examination of acid leaching behaviour of mineral phases from red mud: Recovery of Fe, Al, Ti, and Si. *Minerals Engineering*, 99, 8–18. <u>https://doi.org/10.1016/j.mineng.2016.09.01</u> 2
- Safarzadeh, M. S., Moradkhani, D., & Ojaghi-Ilkhchi, M. (2009). Kinetics of sulfuric acid leaching of cadmium from Cd-Ni zinc plant residues. *Journal of Hazardous Materials*, *163*(2-3), 880–890. <u>https://doi.org/10.1016/j.jhazmat.2008.07.08</u> <u>2</u>
- Silva, J. E., Soares, D., Paiva, A. P., Labrincha, J. A., & Castro, F. (2005). Leaching behaviour of a galvanic sludge in sulphuric acid and ammoniacal media. *Journal of Hazardous Materials*, *121*(1-3), 195-202. <u>https://doi.org/10.1016/j.jhazmat.2005.02.00</u> <u>8</u>
- Singh, J. (2013). *Bioavailability and Leachability of* Heavy Metals during Composting-A Review. <u>www.isca.in</u>
- Smichowski, P., & Marrero, J. (1998). Comparative study to evaluate the effect of different acids on the determination of germanium by hydride generation±inductively coupled plasma atomic emission spectrometry.
- Stanković, J. D., Sabovljević, A. D., & Sabovljević, M. S. (2018). Bryophytes and heavy metals: A review. In *Acta Botanica Croatica* (Vol. 77, Issue 2, pp. 109–118). Sciendo. <u>https://doi.org/10.2478/botcro-2018-0014</u>
- Sulaymon, A. H., Abbas, S. H., Ismail, I. M., Mostafa, T. M., & Sulaymon, A. H. (2014). Biosorption of Heavy Metals: A Review Some of the authors of this publication are also working on these related projects: electrochemical prrojects View project both of them View project Biosorption of Heavy Metals: A Review (Vol. 3, Issue 4). https://www.researchgate.net/publication/26 6795209
- Wang, F., Yang, M., Yang, Y., & Tian, Y. (2024). Synergistic leaching of lithium from claytype lithium ore using sulfuric acid and

oxalic acid. *Applied Clay Science*, 262. https://doi.org/10.1016/j.clay.2024.107623

- Wang, P., Liu, H., Zheng, F., Liu, Y., Kuang, G., Deng, R., & Li, H. (2021). Extraction of Aluminum from Coal Fly Ash Using Pressurized Sulfuric Acid Leaching with Emphasis on Optimization and Mechanism. JOM, 73(9), 2643–2651. https://doi.org/10.1007/s11837-021-04801-z
- Wu, H. Y., & Ting, Y. P. (2006). Metal extraction from municipal solid waste (MSW) incinerator fly ash - Chemical leaching and fungal bioleaching. *Enzyme and Microbial Technology*, 38(6), 839–847. <u>https://doi.org/10.1016/j.enzmictec.2005.08.</u> 012
- Wu, Y., Wang, X., Zhang, X., Lu, Y., Chen, M., Sun, Y., & Ye, P. (2022). Experimental study on remediation of low permeability Cu–Zn contaminated clay by vacuum enhanced leaching combined with EDTA and hydrochloric acid. *Chemosphere*, 298. https://doi.org/10.1016/j.chemosphere.2022. 134332
- Yuliusman, Fajaryanto, R., Nurqomariah, A., & Silvia. (2018). Acid leaching and kinetics study of cobalt recovery from spent lithiumion batteries with nitric acid. E3S Web of Conferences, 67. <u>https://doi.org/10.1051/e3sconf/2018670302</u> 5
- Zhang, F. S., & Itoh, H. (2006). A novel process utilizing subcritical water and nitrilotriacetic acid to extract hazardous elements from MSW incinerator fly ash. *Science of the Total Environment*, *369*(1–3), 273–279. <u>https://doi.org/10.1016/j.scitotenv.2006.04.0</u> <u>15</u>
- Zhang, F. S., & Itoh, H. (2006). Extraction of metals from municipal solid waste incinerator fly ash by hydrothermal process. *Journal of Hazardous Materials*, *136*(3), 663–670. <u>https://doi.org/10.1016/j.jhazmat.2005.12.05</u> <u>2</u>
- Zhang, Y., Jin, B., Huang, Y., Song, Q., & Wang, C. (2019). Two-stage leaching of zinc and copper from arsenic-rich copper smelting hazardous dusts after alkali leaching of arsenic. Separation and Purification Technology, 220, 250–258. https://doi.org/10.1016/j.seppur.2019.03.067

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**RESEARCH ARTICLE** 



## Biodiesel Produced from Sunflower Oil via Heterogeneous Catalysts of Calcium Oxide Prepared from Eggshells Loaded on Barium Oxide

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**Abstract**: In recent years, interest in converting vegetable oils into biodiesel as an environmentally friendly alternative to fossil fuels has increased. Sunflower oil is a vegetable oil that has great potential for biodiesel production. This work explores the use of eggshell-derived calcium oxide along with barium oxide as a heterogeneous catalyst for sunflower oil-based biodiesel generation. The aim of this study was to evaluate the efficiency and feasibility of this catalyst combination in biodiesel synthesis. Experimental tests are conducted to analyze the reaction parameters, including the reaction time, catalyst loading, and temperature, to optimize the biodiesel production process. The properties of the resulting biodiesel are analyzed and compared with standard specifications to assess its quality. The use of heterogeneous catalysts derived from BaO/CaO has shown promising results in transesterification reactions for sunflower oil. The findings of this study provide valuable insights into the potential implementation of these catalyst systems for environmentally friendly biodiesel production.

Keywords: Biodiesel, Eggshells, BaO, Heterogeneous catalyst, Transesterification, Sunflower oils.

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## **1. INTRODUCTION**

The depletion of fossil fuel resources and associated environmental problems have spurred the quest for renewable energy sources, such as biodiesel. Biodiesel is a renewable energy source that can replace conventional diesel fuel. Biomass products are made from biomass sources such as vegetables or animal fats. (Bhatia, 2014, Speight, 2022).

Biodiesel, derived from vegetable oils, is considered a sustainable alternative because of its renewable nature, biodegradability, and reduced emissions. Sunflower oil, which is abundant in many regions, is a viable feedstock for biodiesel production (Bhatia, 2014, Speight, 2022). Studies have estimated that the life cycle emission of greenhouse gases from biodiesel can reach 75% lower than that of petroleum diesel, leading to a reduced carbon footprint (Chen et al., 2018, Gupta et al., 2022, Xu et al., 2022). Moreover, biodiesel has positive impacts on engine performance and longevity. It has higher lubricity than petroleum diesel does, which can improve the lubrication of engine components and reduce wear and tear (Dharma et al., 2016). Transesterification is defined as a chemical reaction that transforms fats and oils into fatty acid methyl esters (biodiesel) (Bhatia, 2014, Couto et al., 2011).

Conventional catalytic processes for the production of biodiesel use homogeneous catalysts, which often require additional purification steps and generate large amounts of waste water (Smith and Notheisz, 1999, Di Serio et al., 2008, Rizwanul Fattah et al., 2020). Heterogeneous catalysts have emerged as a promising alternative to overcome these limitations. Catalysts play a critical role in biodiesel production by accelerating transesterification, increasing conversion efficiency, allowing milder reaction conditions, facilitating continuous production and enabling catalyst reuse (Maheshwari et al., 2022, Neupane, 2022). A variety of catalysts, including enzymatic, base and acidic catalysts, are used in the synthesis of biodiesel. Each type of catalyst has a different mechanism of action and a range of advantages and disadvantages (Mandari and Devarai, 2022, Changmai et al., 2020, Di Serio et al., 2008, Ma, 1999).

The production process is more efficient when heterogeneous catalysts are used since they are easily separated from biodiesel and are insoluble in the reaction mixture (Yan et al., 2010). Heterogeneous catalysts facilitate the transesterification reaction by providing active sites on their surface for the reaction to occur. These active sites promote the interaction between triglycerides and alcohol, leading to the formation of fatty acid methyl esters (FAMEs). The catalysts can be tailored to increase their activity, selectivity, and stability in biodiesel production (Védrine, 2017, Yan et al., 2010, Zabeti et al., 2009). In recent years, several heterogeneous catalysts have been extensively studied for their potential applications in biodiesel synthesis (Mahdi et al., 2023, Rizwanul Fattah et al., 2020, Laskar et al., 2018, Roschat et al., 2016). One widely investigated heterogeneous catalyst is based on solid acids. These catalysts are typically composed of an acidic material supported on a solid substrate, such as silica or alumina. Solid acid catalysts offer numerous advantages, including high activity, reusability, and resistance to water and impurities.

The unique features and high catalytic activity of alkali earth metal oxide catalysts have demonstrated considerable potential in the generation of biodiesel (Sulaiman et al., 2020). These catalysts, including calcium oxide, magnesium oxide, strontium oxide and barium oxide, offer several advantages in the transesterification process because they exhibit strong basicity, which is essential for the transesterification reaction (Li et al., 2022, Sulaiman et al., 2020, Roschat et al., 2016, Anastopoulos et al., 2013b, Verziu et al., 2011). Research has demonstrated that alkaline earth metal oxide catalysts exhibit high catalytic activity, leading to faster reaction rates and higher biodiesel yields. Triglycerides are easily converted to fatty acid methyl esters (FAMEs) via the use of these catalysts (Ma, 1999, Leung et al., 2010, Rizwanul Fattah et al., 2020). The strong basic sites on the catalyst surface promote the breaking of ester bonds, resulting in efficient transesterification reactions. Furthermore, alkali earth metal oxide catalysts are relatively inexpensive, readily available, and environmentally friendly. CaO, for example, can easily be derived from calcium-rich sources, such as limestone, also known as quicklime, and is one of the most widely used alkali earth metal oxide catalysts in biodiesel production. CaO has strong basic properties, allowing it to efficiently catalyze the transesterification reaction. It provides active sites on its surface for the interaction between triglycerides and alcohol, promoting the formation of fatty acid methyl esters (FAMEs) and glycerol (Kesic et al., 2016). Similarly, MgO and SrO can be obtained from abundant sources, further increasing their economic viability (Rasouli and Esmaeili, 2019, Hu et al., 2023, Verziu et al., 2011).

As has been demonstrated in numerous studies, CaO catalyst has been demonstrated to effectively catalyze the transesterification of high-grade or vegetable oil. In order to further enhance the catalytic properties of BaO, an attempt was made to combine it with CaO. It has been demonstrated that barium oxide catalysts display catalytic activity in transesterification processes, attributed to their high basicity (Ghanbari Zadeh Fard et al., 2019, Hanif et al., 2022, Ivanova et al., 2012, Martinez-Guerra and Gude, 2014, Olutoye et al., 2016, Sahani et al., 2019, Singh et al., 2019, Yusuff et al., 2021, Chew et al., 2017, Patil, 2012, Al-Abbasi et al., 2023). The transesterification of palm cooking oil using barium-containing titanates, including Ba-TiO<sub>3</sub> and Ba<sub>2</sub>NiTi<sub>5</sub>O<sub>13</sub>, as well as their Na-doped analogues, was investigated by Chew et al. (Chew et al., 2017). The efficacy of microwave irradiation in biodiesel production from waste cooking oil was evaluated through a microwave-assisted catalytic transesterification process utilising BaO and KOH (Patil, 2012).

Recently, we have successfully synthesized BaO nanoparticles via the sol-gel method and examined their catalytic performance on the transesterification of sunflower oil (Al-Abbasi et al., 2023). To date, no studies have been conducted on the transesterification of sunflower oil using barium oxide nanoparticles supported by CaO from natural resources. Continuing our previous study of the chemistry of metals and their use in various industrial applications (Belkher, 2019, Khalifa, 2018, Al-Abbasi et al., 2023, Al-abbasi et al., 2022, Al-abbasi et al., 2012, Al-abbasi and Kassim, 2011), this research aimed to investigate the efficiency of CaO, BaO and CaO/BaO catalysts in converting sunflower oil into biodiesel while also analyzing the reaction parameters that can impact biodiesel yield, including reaction time, catalyst loading, and temperature. Analyses were carried out on the generated biodiesel to determine its density, kinematic viscosity, and acid value.

#### 2. EXPERIMENTAL SECTION

#### 2.1 Materials

All the chemicals were utilized just as received and required no additional purification. Citric acid (> 99.5%), barium nitrate (> 96%) and EDTA (> 99%) were used. Sunflower oil (SFO) was provided by Sabha city local market. Chicken eggshells were collected as waste from the house used.

#### 2.2 Preparation

# 2.2.1 Preparation of the Eggshell Waste-Derived CaO Catalyst

The CaO catalyst can be produced via calcination, in which the dried eggshells are calcined for four hours at 1000 °C. The product was obtained as a white powder. The calcined samples were kept in a closed vessel.

## 2.2.2 Preparation of BaO nanoparticles

The sol-gel approach was used for generating BaO, and the procedure was described in our recent publication (Al-Abbasi et al., 2023, Salim et al., 2022).

#### 2.2.3 Preparation of BaO/CaO NPs

The sol-gel technique, which is similar to BaO synthesis, was used to produce BaO/CaO (Al-Abbasi et al., 2023). A 1:1:1:1.5 molar ratio of calcium oxide from calcined egg shells, barium nitrate, EDTA, and citric acid was combined with deionized water. The end product was dried overnight at 60 °C to produce a dense black gel. After that, the gel was calcined at 1000 °C until it became a white powder.

#### 2.2.4 Biodiesel preparation

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#### 2.3 Characterization Methods

Infrared data were collected in the 400-4000 cm<sup>-1</sup> wavenumber range using a Bruker (Germany). An NEX QC-JSM-6290LV analyzer was used to carry out the EDXRF analysis. High-performance liquid chromatography (HPLC) analyses were performed with a KNAUER AZURA HPLC instrument with a DAD 6.1 UV-Vis detector and a Eurospher II 100-5 C18 column. The flow rate was 1 mL/min, the column temperature was maintained at 40 °C, and the UV detector wavelength was set at 205 nm. The mobile phase was composed of polar mixtures of water and acetonitrile.

#### 2.4. Physical Properties of Biodiesel

2.4.1 Acid Value Test

The acid content was calculated via the following formula (Eq. 2):

$$pH = \frac{(b-a) \times (x) \times N}{W}$$
(2)

where N is the standard alkali's normality, W is the sample weight (g), x is the molar mass of KOH, b is the standard alkali used for the sample's titration (mL), and a is the standard alkali used for the blank's titration (mL).

#### 2.4.2 Determination of water content

The glass beaker was washed well with distilled water and dried in a desiccator. W<sub>1</sub> was weighed, 10 ml of oil was placed in the beaker, W<sub>2</sub> was Previously published papers (Salim et al., 2022, Al-Abbasi et al., 2023) described the process of preparing biodiesel. Typically, methanol was added along with the selected catalyst (BaO, CaO, or BaO/CaO) in a two-necked flask connected to a refluxing apparatus, and sunflower oil was added. After the transesterification reaction was complete, the mixture was centrifuged at 5000 rpm for 15 minutes to remove the catalyst particles. This was followed by washing the solution with hot distilled water. The yield was calculated via Equation (1):

$$Wield(\%) = \frac{Weight of biodiesel product}{weight of SFO oil} \times 100$$
(1)

weighed, the cup was placed in the desiccator for 15 minutes,  $W_3$  and the cup were returned to the desiccator for another 15 minutes, the weight was taken as W<sub>4</sub>, the cup was returned to the dryer for another 15 minutes, and the weight was taken. W<sub>5</sub>, the weight level means that the oil does not contain any moisture. The moisture content is estimated from the following law:

Water ratio = 
$$\frac{Wi - Wf}{Wi}$$
 100%(3)

## **3. RESULTS AND DISCUSSION**

### 3.1 Thermal Decomposition of Eggshell Powder

The thermal decomposition of eggshell powder refers to the process by which eggshell powder decomposes when subjected to high temperatures. Carbon dioxide  $(CO_2)$  gas and calcium oxide (CaO)are the products of the thermal decomposition of calcium carbonate (CaCO<sub>3</sub>). This reaction proceeds in accordance with the following equation:

$$CaCO_3 \rightarrow CO_2 + CaO$$
 (3)

The temperature at which this decomposition occurs typically ranges between 900 °C and 1000 °C. Overall, the thermal decomposition of eggshell powder provides a means to separate the calcium carbonate component and obtain calcium oxide, which has utility in a range of industries (Figure 1).



Figure 1: a) Raw eggshells, b) powdered eggshells, c) 1-hour calcined eggshell, and d) CaO oxide powder.

## 3.2 Characterization of the BaO Catalyst

Characterization of the synthesized catalyst was performed via techniques such as energy-disper-

sive X-ray spectroscopy (EDXRF) and infrared (IR) spectroscopy. EDXRF analysis was used to determine the CaO, BaO and CaO/BaO catalysts after synthesis and calcination (Titus et al., 2019, Scimeca et al., 2018). The results of the EDXRF analysis are shown in Figure 2, and the compositions of the samples are presented in Table 1. The observed and calculated values for the metal oxide catalysts used were similar, as shown in Table 1. On the basis of the EDXRF analysis, the CaO catalyst from the eggshell was determined to be composed of 72.3% w/w CaO, 89.3% w/w BaO, 19.4% w/w CaO and 64.0% w/w BaO. Thus, eggshell material can be utilized as a raw material for CaO catalyst synthesis. The spectrum depicted in Figure 2 shows the EDXRF readings for Ca ( $K\alpha = 3.692$  keV,  $K\beta$  = 4.012 keV), which are consistent with findings from previous research (Wicaksono and Kusumaningtyas, 2019, Lignon et al., 2017). However, the results of earlier studies (Al-Abbasi et al., 2023) were compatible with the EDXRF values for Ba Kα (31.81 and 32.19 KeV), Ba Lα (4.46 and 4.83 KeV), Ba Lβ (4.93 and 5.16 KeV), and Ba kβ (36.37 and 73.35 KeV) at high Z (Renukadevi et al., 2020).

Figure 3 displays the FT-IR pattern of the prepared 1:1 BaO/CaO catalyst, the obtained BaO, and the

eggshell-derived CaO over the 400-4000 cm<sup>-1</sup> range. The interpretation of the FTIR spectra of BaO would be similar to the interpretation mentioned above for CaO. The existence of peaks between 500 and 600 cm<sup>-1</sup>, which are suggestive of the M-O stretch, which is the stretching vibration of the metal-oxygen bond, may indicate the presence of characteristic peaks associated with the metal-oxide structure in the spectrum. (Manauwar Ali and Nusrat, 2021, Jitjamnong et al., 2019, Al-abbasi et al., 2010, Almutaleb and Alabbasi, 2023).

Furthermore, the bending vibrations of the oxygen atoms in the lattice may be represented by peaks in the 600-900 cm<sup>-1</sup> range (Manauwar Ali and Nusrat, 2021, Renukadevi et al., 2020, Sundharam et al., 2017). Water absorption on the synthesized catalyst surface was linked to two absorption bands at 3640 cm<sup>-1</sup> and 1400 cm<sup>-1</sup>, which correspond to the OH bond stretching and bending modes of vibrations, respectively (Jitjamnong et al., 2019, Boro et al., 2011, Al-Abbasi et al., 2023). It was determined that the bending mode of the OH group of physically adsorbed moisture on the surface was responsible for the wider band at approximately 3423 cm<sup>-1</sup> (Boro et al., 2011, Maneerung et al., 2016, Al-Abbasi et al., 2023).

**Table 1:** Elemental analysis of the metal oxide catalysts.

Catalyst	Ca %	Ba %
-	(Calc.)	(Calc.)
BaO	- (/)	89.3 (89.6)
CaO	72.3 (71.4)	- (/)
BaO/CaO	19.4 (19.1)	64.0 (65.6)



Figure 2: Catalyst EDX signals.



Figure 2: IR spectra of prepared catalyst.

## 3.2. Characterization of Prepared Biodiesel

The chemical constitution of the biodiesel was ascertained via high-performance liquid chromatography (HPLC). Retention time information was used to identify a number of FAMEs. The biodiesel HPLC spectrum revealed seven primary signs (Figure 4). Software for library matching was used to assess each signal. Linoleic, oleic, palmitic, and stearic acids are the most common fatty acids (Salim et al., 2022, Anastopoulos et al., 2013a, Anastopoulos et al., 2013b, Al-Abbasi et al., 2023).



Figure 4: HPLC chromatogram from an experimental run.

The infrared (IR) spectra of biodiesel can provide information about its molecular structure and functional groups. The mid-infrared (4000–400 cm<sup>-1</sup>) IR spectra, which correspond to the molecular vibrational frequencies, are shown in Figure 5. Carbonyl (C=O) stretching, ester (C-O-C) stretching, and methylene (CH<sub>2</sub>) bending are often encountered as functional groups in biodiesel. By analyzing the FTIR spectra of the FAME fuel in Figure 5, various functional groups present in the fuel can be identified. The absorption peak at approximately 1740-1760 cm<sup>-1</sup> indicates the presence of carbonyl (C=O) stretching vibrations, which are characteristic of esters. Peaks attributed to C-H vibrations are found between 2800 and 3000 cm-1 (Wembabazi et al., 2015, Al-Abbasi et al., 2023). Additional biodiesel peak signals were detected at a wavenumber of 1099 cm-1 (C-O), which was similar to what was previously reported (Wembabazi et al., 2015, Yuan et al., 2014, Siatis et al., 2006).



Figure 5: FT-IR spectra of the FAME samples.

### 3.3 Transesterification Optimization Conditions

Researchers have identified key factors that influence the transesterification process: the methanolto-oil ratio, catalyst concentration, temperature and reaction time. These factors were varied at different levels to determine their individual and combined effects on biodiesel yield. Initially, in our previously published research, the methanol-to-oil ratio was optimized by the use of barium oxide. The ideal methanol-to-oil ratio was found to be 20:1 according to tests conducted to determine the effect on biodiesel yield (Al-Abbasi et al., 2023). Thus, in this continued research, the methanol-to-oil ratio was fixed at 20:1 in all the runs (Table 2).

Table 2: FAME yield optimization values.

Exp. No	Time	Temp	Cata.	Yield (%)		
	(min)	(°C)	(W%)	BaO	CaO	CaO/ BaO
1	60	70	4.7	61.3	80.2	83.04
2	120	70	4.7	66.8	80.58	83.87
3	180	70	4.7	72.53	81.25	85.95
4	240	70	4.7	78.38	86.03	87.77
5	180	65	4.7	63.24	79.12	82.5
6	180	75	4.7	68.45	66.01	62.65
7	180	70	1.58	68.15	74.67	78.28
8	180	70	3.15	70.67	76.98	82.48
9	180	70	4.7	72.53	81.25	85.95
10	180	70	6.3	74.82	83.2	88.48

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#### 3.4.1. Temperature

The reaction rate, yield, and selectivity of the transesterification process are directly influenced

by the temperature at which the reaction is carried out.



Figure 6: FAME yield change with temperature.

Research has shown that increasing the temperature generally enhances the reaction rate of transesterification (Figure 6). This is because higher temperatures increase the kinetic energy of the reactant molecules, leading to an increased frequency of collisions and, subsequently, a higher rate of reaction. However, there is an optimal temperature range for transesterification reactions. The reaction rate may begin to decline after this optimum range because of the thermal degradation of the reactants or the production of undesirable byproducts. The transesterification procedure was carried out at three different temperatures-65, 70, and 75 °C-to examine the effect of temperature on the FAME yield. During the optimization process, the following parameters were maintained constant: a time interval of 180 minutes, a catalyst quantity of 4.7%, and a methanol/oil ratio of 20:1. The efficiency of methyl ester conversion is illustrated in Figure 6. With all the tested catalysts, the highest conversion efficiencies of 72.53%, 81.25%, and 87.77% were achieved at 70°C for BaO, CaO, and BaO/CaO catalysts, respectively.

#### 3.4.2. Effect of catalyst concentration

An experiment was carried out with a 12:1 methanol-to-oil ratio at 65 °C for three hours. This result is exemplified in Figure 7, where a lower catalyst concentration of 1.58% offers lower biodiesel yields of 68.15%, 74.67%, 78.28% and 83.49% for the BaO, CaO, and BaO/CaO catalysts, respectively. Increasing the catalyst concentration to 6.3% also increased the FAME yield by 74.82%, 83.2%, 88.48% and 92.45% for the BaO, CaO, and BaO/CaO catalysts, respectively. Several studies have examined how the concentration of alkali earth catalysts affects the transesterification reaction. (Anastopoulos et al., 2013b, Arun et al., 2017, Kouzu et al., 2008, Roschat et al., 2016, Verziu et al., 2011). Increasing the catalyst concentration often results in increased reaction rates and conversions (Antunes et al., 2008).



Figure 7: FAME yield under catalyst concentration optimization.

#### 3.4.3. The effect of time

The reaction time can significantly affect the transesterification reaction. Figure 8 shows that longer reaction times (up to 240 min) led to higher conversion rates and improved biodiesel yields by all the used catalysts, whose yield started to decrease after 180 min, indicating that an optimal reaction time exists for this catalyst to achieve maximum conversion.



Figure 8: FAME yield under time optimization.

A longer reaction time can generally lead to higher conversion rates and better yields. However, the relationship between reaction time and reaction kinetics is complex and may depend on various factors, such as reaction conditions, catalyst type, reactant concentrations, and temperature (Anastopoulos et al., 2013b, Arun et al., 2017, Verziu et al., 2011).

## 3.5 Physicochemical Properties of Biodiesel

The physicochemical properties of biodiesel refer to the characteristics and behavior of biodiesel from a physical and chemical perspective. The characteristics of the biodiesel were evaluated according to ASTM 6750.820 – 0.8452. The biodiesel quality was evaluated on the basis of the ASTMglobal biodiesel standards (Table 3).

The biodiesel density refers to the mass of biodiesel per unit volume. The estimated densities were 0.904, 0.909 and 0.908 g/cm<sup>3</sup>. The density of fuel is affected by a number of parameters, such as unsaturation, which causes the density to increase with unsaturation, and chain length, which causes the fuel density to decrease with chain length. (Salim et al., 2022). Viscosity measures the

fluidity or thickness of biodiesel. It affects the fuel's ability to atomize and vaporize during combustion, as well as its flow characteristics in fuel delivery systems. The estimated viscosities at 100°C were 5.58, 3.601 and 3.577 cST for BaO, CaO and CaO/BaO, respectively, which are comparable to the international standards (Keera et al., 2018, Salim et al., 2022).

The acid content and water content are important parameters used to assess the quality of biodiesel. The quantity of free fatty acids in biodiesel fuel is recognized as the acid value of biodiesel. The estimated acid concentrations were 1.052, 0.974 and 1.066 mg KOH/g for biodiesel produced by the BaO, CaO and CaO/BaO catalysts, respectively, which are higher than the ASTM international standards. The presence of free fatty acids is considered to indicate high acidity. The water content of biodiesel refers to the amount of water present in the biodiesel fuel. The estimated water percentages were 0.001, 0.01 and 0.1 for biodiesel produced by the BaO, CaO and CaO/BaO catalysts, respectively, which are comparable to the ASTM-6750.820 - 0.8452 standards.

		Standard	Results			
ASTM Test	Unit	ASTM-6750. 820 –0.8452	Sunflower oil	BaO	CaO	CaO/BaO
Specific Grav- ity15@ °C)60°F)	-	820 - 845.2	0.923	0.904	0.909	0.908
Density 15@ °C	kg/L	820 - 845.2	0.92	0.902	0.907	0.908
Kinematic Vis- cosity 100@°C	cST	1.9 - 6.0	6.39	5.58	3.601	3.557
Water Content	%	< 0.05	0.32	0.1	0.01	0.012
Acid Value	mg/g	0.50	0.432	1.105	0.974	1.066

Table 3: Physicochemical properties of the biofuel.

## 4. CONCLUSION

This research aimed to provide valuable insights into the conversion of sunflower oil into biodiesel via the use of heterogeneous CaO, BaO and CaO/ BaO catalysts. Thus, the catalytic activities of three different catalysts, CaO, BaO, and CaO/BaO, for the production of biodiesel as heterogeneous catalysts were investigated. Chicken eggshell waste was calcined at 1000 °C to yield a CaO catalyst for the synthesis of biodiesel. The tested catalysts were characterized by EDXRF and IR spectroscopy and then evaluated for successful transesterification with methanol. In addition, IR spectroscopy and HPLC were used to investigate the biodiesel that was produced. The influences of the reaction time, reaction temperature, and catalyst concentration on the biofuel yield were explored. The addition of eggshell CaO to BaO resulted in an increase in yield to approximately 87.7% compared with that of the BaO catalyst (78.38%) under the same experimental conditions: a reaction time of 4 h, a reaction temperature of 70°C, a methanol-to-oil ratio of 20:1, and a catalyst loading of 4.6 wt%. The ability of the tested catalysts to transcribe was in the order of BaO < CaO < CaO/BaO. The generated biodiesel was tested against relevant international standards, indicating that it fits certain criteria and is therefore a biocompatible substitute for regular diesel. The use of discarded eggshells was one of the key benefits of this study. Future research can examine the effects of additional natural sources of calcium oxide, such as bone and eggshells, on the transesterification of plant-based oils.

## **5. CONFLICT OF INTEREST**

No conflict of interest.

## 6. ACKNOWLEDGMENTS

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## 7. REFERENCES

- AL-ABBASI, A., ALMAHDI, F., ALMAKY, M., IZRIQ, R., MILAD, A., SALIM, S. & NAJAR, A. 2023. BaO as a heterogeneous nanoparticle catalyst in oil transesterification for the production of FAME fuel. Inorganic Chemistry Communications, 158, 111620.
- AL-ABBASI, A. A. & KASSIM, M. B. 2011. 1-Benzoyl-3-ethyl-3-phenylthiourea. Acta Crystallographica Section E, 67, o611.
- AL-ABBASI, A. A., MOHAMED TAHIR, M. I. & KASSIM, M. B. 2012. N-(Pyrrolidin-1ylcarbothioyl)benzamide. Acta Crystallographica Section E, 68, o201.
- AL-ABBASI, A. A., TAHIR, M. I. M., KAYED, S. F. & KASSIM, M. B. 2022. Synthesis, characterisation and biological activities of mixed ligand oxovanadium (IV) complexes derived from N,N-diethyl-N'-para-substituted-benzoylthiourea and hydrotris(3,5dimethylpyrazolyl)borate. Applied Organometallic Chemistry, 36, e6607.
- AL-ABBASI, A. A., YARMO, M. A. & KASSIM, M. B. 2010. N-[(Piperidin-1-yl)carbothioyl]benzamide. Acta Crystallographica Section E, 66, 02896.
- ALMUTALEB, A. A. A. & ALABBASI, A. A. 2023. Synthesis, characterization and computational studies for (2'S\*,3R\*,3'S\*,8a'R\*)-2',3'bis(ethoxycarbonyl)-2-oxo-2',3'-dihydro-8a'Hspiro[indoline-3,1'-indolizine]-6'-carboxylic acid and some derivatives. Journal of Physical Organic Chemistry, 36, e4452.
- ANASTOPOULOS, G., DODOS, G., KALLIGEROS, S. & ZANNIKOS, F. 2013a. Methanolysis of sunflower oil and used frying oil using LiNO3/ CaO as a solid base catalyst. International Journal of Ambient Energy, 34.
- ANASTOPOULOS, G., DODOS, G. S., KALLIGEROS, S. & ZANNIKOS, F. 2013b. Methanolysis of sunflower oil and used frying oil using LiNO3/CaO as a solid base catalyst. International Journal of Ambient Energy, 34, 73-82.

ANTUNES, W., VELOSO, C. & HENRIQUES, C. 2008. Transesterification of soybean oil with methanol catalyzed by basic solids. Catalysis Today - CATAL TODAY, 133, 548-554.

- ARUN, S. B., SURESH, R., YATISH, K. V., OMKARESH, B. R. & CHANNA KESHAVA NAIK, N. 2017. Use of CaO and Na3PO4 Catalysts in the Synthesis of Biodiesel and Investigation of Fuel Properties. Materials Today: Proceedings, 4, 1111-11117.
- BELKHER, N., AL-ABBASI, A. AND ZIDAN, M. 2019 Potentiometric Studies on Stability Constant of the Complexes of SomeEssential Transition Metal Ions with L-Valine. Journal of Pure & Applied Science 13, 59-63.
- BHATIA, S. C. 2014. 22 Biodiesel. In: BHATIA, S. C. (ed.) Advanced Renewable Energy Systems. Woodhead Publishing India.
- BORO, J., THAKUR, A. J. & DEKA, D. 2011. Solid oxide derived from waste shells of Turbonilla striatula as a renewable catalyst for biodiesel production. Fuel Processing Technology, 92, 2061-2067.
- CHANGMAI, B., VANLALVENI, C., INGLE, A. P., BHA-GAT, R. & ROKHUM, S. L. 2020. Widely used catalysts in biodiesel production: a review. RSC Advances, 10, 41625-41679.
- CHEN, R., QIN, Z., HAN, J., WANG, M., TAHERIPOUR, F., TYNER, W., O'CONNOR, D. & DUFFIELD, J. 2018. Life cycle energy and greenhouse gas emission effects of biodiesel in the United States with induced land use change impacts. Bioresource Technology, 251, 249-258.
- CHEW, K. Y., TAN, W. L., ABU BAKAR, N. H. H. & ABU BAKAR, M. 2017. Transesterification of palm cooking oil using barium-containing titanates and their sodium doped derivatives. International Journal of Energy and Environmental Engineering, 8, 47-53.
- COUTO, S., MATA, T. M., MARTINS, A. A., MOURA, B., MAGALHÃES, J. & CAETANO, N. S. 2011. Design and Simulation of Eco-Efficient Biodiesel Manufacture. In: PISTIKOPOULOS, E. N., GEORGIADIS, M. C. & KOKOSSIS, A. C. (eds.) Computer Aided Chemical Engineering. Elsevier.
- DHARMA, S., ONG, H. C., MASJUKI, H. H. & SE-BAYANG, A. 2016. An overview of engine durability and compatibility using biodieselbioethanol-diesel blends in compression-ignition engines. Energy Conversion and Management, 128.
- DI SERIO, M., TESSER, R., PENGMEI, L. & SANTACE-SARIA, E. 2008. Heterogeneous Catalysts for Biodiesel Production. Energy & Fuels, 22, 207-217.

- GHANBARI ZADEH FARD, R., JAFARI, D., PALIZIAN, M. & ESFANDYARI, M. 2019. Biodiesel production from beef tallow using the barium oxide catalyst. Reaction Kinetics, Mechanisms and Catalysis, 128, 723-738.
- GUPTA, R., MCROBERTS, R., YU, Z., SMITH, C., SLOAN, W. & YOU, S. 2022. Life cycle assessment of biodiesel production from rapeseed oil: Influence of process parameters and scale. Bioresource Technology, 360, 127532.
- HANIF, S., ALSAIARI, M., AHMAD, M., SULTANA, S., ZAFAR, M., ROZINA, HARRAZ, F. A., ALHARBI, A. F., ABAHUSSAIN, A. A. M. & AHMAD, Z. 2022. Membrane reactor based synthesis of biodiesel from Toona ciliata seed oil using barium oxide nano catalyst. Chemosphere, 308, 136458.
- HU, M., PU, J., QIAN, E. W. & WANG, H. 2023.
   Biodiesel Production Using MgO-CaO Catalysts via Transesterification of Soybean Oil: Effect of MgO Addition and Insights of Catalyst Deactivation. BioEnergy Research.
- IVANOVA, A. S., SHERSTYUK, O. V., BUKHTI-YAROVA, M. V., KUKUSHKIN, R. G., MATVIENKO, L. G., PLYASOVA, L. M., KAICHEV, V. V., SIMONOV, A. N. & YAKOVLEV, V. A. 2012. Performance of Bacontaining catalysts in the transesterification reaction of rapeseed oil with methanol under flow conditions. Catalysis Communications, 18, 156-160.
- JITJAMNONG, J., LUENGNARUEMITCHAI, A., SAMAN-WONGA, N. & CHUAYKARN, N. 2019. Biodiesel Production from Canola Oil and Methanol Using Ba Impregnated Calcium Oxide with Microwave Irradiation-Assistance. Chiang Mai Journal of Science, 46, 987-1000.
- KEERA, S., EL SABAGH, S. & TAMAN, A. J. E. J. O. P. 2018. Castor oil biodiesel production and optimization. Egyptian journal of petroleum, 27, 979-984.
- KESIC, Z., LUKIĆ, I., ZDUJIĆ, M., MOJOVIC, L. & SKALA, D. 2016. Calcium oxide based catalysts for biodiesel production: A review. Chemical Industry and Chemical Engineering Quarterly, 22, 10-10.
- KHALIFA, S., AL-ABBASSI, A., SULIMAN, M. 2018. Adsorption and Corrosion Inhibition of Mild Steel in Acidic Media by Expired Pharmaceutical Drug. Journal of Pure & Applied Sciences, 17, 1-6.
- KOUZU, M., KASUNO, T., TAJIKA, M., SUGIMOTO, Y., YAMANAKA, S. & HIDAKA, J. 2008. Calcium oxide as a solid base catalyst for transesteri-

fication of soybean oil and its application to biodiesel production. Fuel, 87, 2798-2806.

- LASKAR, I. B., RAJKUMARI, K., GUPTA, R., CHATTER-JEE, S., PAUL, B. & ROKHUM, S. L. 2018. Waste snail shell derived heterogeneous catalyst for biodiesel production by the transesterification of soybean oil. RSC Advances, 8, 20131-20142.
- LEUNG, D. Y., WU, X. & LEUNG, M. J. A. E. 2010. A review on biodiesel production using catalyzed transesterification. 87, 1083-1095.
- LI, Y., ZHANG, Y., QIAN, K. & HUANG, W. 2022. Metal-Support Interactions in Metal/Oxide Catalysts and Oxide-Metal Interactions in Oxide/Metal Inverse Catalysts. ACS Catalysis, 12, 1268-1287.
- LIGNON, G., BERÈS, F., QUENTRIC, M., ROUZIÈRE, S., WEIL, R., DE LA DURE-MOLLA, M., NAVEAU, A., KOZYRAKI, R., BERDAL, A. & DESSOMBZ, A. 2017. FAM20A Gene Mutation: Amelogenesis or Ectopic Mineralization? Frontiers in Physiology, 1, 267.
- MA, F., HANNA, MILFORD A. 1999. Biodiesel production: a review Bioresource Technology, 70, 1-15.
- MAHDI, H. I., RAMLEE, N. N., DA SILVA DUARTE, J. L., CHENG, Y.-S., SELVASEMBIAN, R., AMIR, F., DE OLIVEIRA, L. H., WAN AZELEE, N. I., MEILI, L. & RANGASAMY, G. 2023. A comprehensive review on nanocatalysts and nanobiocatalysts for biodiesel production in Indonesia, Malaysia, Brazil and USA. Chemosphere, 319, 138003.
- MAHESHWARI, P., HAIDER, M. B., YUSUF, M., KLE-MEŠ, J. J., BOKHARI, A., BEG, M., AL-OTHMAN, A., KUMAR, R. & JAISWAL, A. K. 2022. A review on latest trends in cleaner biodiesel production: Role of feedstock, production methods, and catalysts. Journal of Cleaner Production, 355, 131588.
- MANAUWAR ALI, A. & NUSRAT, J. 2021. Structural and Optical Properties of BaO Nanoparticles Synthesized by Facile Co-precipitation Method. Materials Highlights, 2, 23-28.
- MANDARI, V. & DEVARAI, S. K. 2022. Biodiesel Production Using Homogeneous, Heterogeneous, and Enzyme Catalysts via Transesterification and Esterification Reactions: a Critical Review. Bioenergy Res, 15, 935-961.
- MANEERUNG, T., KAWI, S., DAI, Y. & WANG, C.-H. 2016. Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure. Energy Conversion and Management, 123, 487-497.

- MARTINEZ-GUERRA, E. & GUDE, V. G. 2014. Transesterification of used vegetable oil catalyzed by barium oxide under simultaneous microwave and ultrasound irradiations. Energy Conversion and Management, 88, 633-640.
- NEUPANE, D. 2022. Biofuels from Renewable Sources, a Potential Option for Biodiesel Production. Bioengineering (Basel), 10.
- OLUTOYE, M. A., WONG, S. W., CHIN, L. H., AMANI, H., ASIF, M. & HAMEED, B. H. 2016. Synthesis of fatty acid methyl esters via the transesterification of waste cooking oil by methanol with a barium-modified montmorillonite K10 catalyst. Renewable Energy, 86, 392-398.
- PATIL, P., GUDE, V., REDDY, H., MUPPANENI, T. AND DENG, S. 2012. Biodiesel Production from Waste Cooking Oil Using Sulfuric Acid and Microwave Irradiation Processes. Journal of Environmental Protection, 3, 107-113.
- RASOULI, H. & ESMAEILI, H. 2019. Characterization of MgO nanocatalyst to produce biodiesel from goat fat using transesterification process. 3 Biotech, 9, 429.
- RENUKADEVI, R., SUNDARAM, R. & KASINATHAN, K. 2020. Barium Oxide nanoparticles with robust catalytic, photocatalytic and humidity sensing properties. Journal of Nanostructures, 10, 167-176.
- RIZWANUL FATTAH, I. M., ONG, H. C., MAHLIA, T. M. I., MOFIJUR, M., SILITONGA, A. S., RAH-MAN, S. M. A. & AHMAD, A. 2020. State of the Art of Catalysts for Biodiesel Production. Frontiers in Energy Research, 8.
- ROSCHAT, W., SIRITANON, T., YOOSUK, B. & PRO-MARAK, V. 2016. Biodiesel production from palm oil using hydrated lime-derived CaO as a low-cost basic heterogeneous catalyst. Energy Conversion and Management, 108, 459-467.
- SAHANI, S., ROY, T. & CHANDRA SHARMA, Y. 2019. Clean and efficient production of biodiesel using barium cerate as a heterogeneous catalyst for the biodiesel production; kinetics and thermodynamic study. Journal of Cleaner Production, 237, 117699.
- SALIM, S. M., IZRIQ, R., ALMAKY, M. M. & AL-AB-BASSI, A. A. 2022. Synthesis and characterization of ZnO nanoparticles for the production of biodiesel by transesterification: Kinetic and thermodynamic studies. Fuel, 321, 124135.
- SCIMECA, M., BISCHETTI, S., LAMSIRA, H. K., BON-FIGLIO, R. & BONANNO, E. 2018. Energy Dis-

persive X-ray (EDX) microanalysis: A powerful tool in biomedical research and diagnosis. Eur J Histochem, 62, 2841.

- SIATIS, N., KIMBARIS, A., PAPPAS, C., TARANTILIS, P. & POLISSIOU, M. J. J. O. T. A. O. C. S. 2006. Improvement of biodiesel production based on the application of ultrasound: monitoring of the procedure by FTIR spectroscopy. 83, 53-57.
- SINGH, R., KUMAR, A. & CHANDRA SHARMA, Y. 2019. Biodiesel Production from Microalgal Oil Using Barium-Calcium-Zinc Mixed Oxide Base Catalyst: Optimization and Kinetic Studies. Energy & Fuels, 33, 1175-1184.
- SPEIGHT, J. G. 2022. Encyclopedia of Renewable Energy, Wiley.
- SULAIMAN, N. F., HASHIM, A. N. N., TOEMEN, S., ROSID, S. J. M., MOKHTAR, W. N. A. W., NADARAJAN, R. & BAKAR, W. A. W. A. 2020. Biodiesel production from refined used cooking oil using co-metal oxide catalyzed transesterification. Renewable Energy, 153, 1-11.
- SUNDHARAM, E., JEEVARAJ, A. & CHINNUSAMY, C. 2017. Effect of Ultrasonication on the Synthesis of Barium Oxide Nanoparticles. Journal of Bionanoscience, 11, 310-314.
- TITUS, D., JAMES JEBASEELAN SAMUEL, E. & ROOPAN, S. M. 2019. Chapter 12 - Nanoparticle characterization techniques. In: SHUKLA, A. K. & IRAVANI, S. (eds.) Green Synthesis, Characterization and Applications of Nanoparticles. Elsevier.
- VÉDRINE, J. C. 2017. Heterogeneous Catalysis on Metal Oxides. Catalysts, 7, 341.
- VERZIU, M., COMAN, S. M., RICHARDS, R. & PARVULESCU, V. I. 2011. Transesterification

of vegetable oils over CaO catalysts. Catalysis Today, 167, 64-70.

- WEMBABAZI, E., MUGISHA, P. J., RATIBU, A., WENDIRO, D. & KYAMBADDE, J. J. J. O. S. 2015. Spectroscopic analysis of heterogeneous biocatalysts for biodiesel production from expired sunflower cooking oil. 2015.
- WICAKSONO, D. & KUSUMANINGTYAS, R. 2019. Synthesis of ZnO/CaO Catalyst from Eggshell Waste for Biodiesel Production. Jurnal Bahan Alam Terbarukan, 8, 65-71.
- XU, H., OU, L., LI, Y., HAWKINS, T. R. & WANG, M. 2022. Life Cycle Greenhouse Gas Emissions of Biodiesel and Renewable Diesel Production in the United States. Environmental Science & Technology, 56, 7512-7521.
- YAN, S., DIMAGGIO, C., MOHAN, S., KIM, M., SAL-LEY, S. O. & NG, K. Y. S. 2010. Advancements in Heterogeneous Catalysis for Biodiesel Synthesis. Topics in Catalysis, 53, 721-736.
- YUAN, T., AKOCHI-KOBLE, E., PINCHUK, D., VAN DE VOORT, F. R. J. I. J. O. R. E. & BIOFUELS 2014. FTIR on-line monitoring of biodiesel transesterification. 2014, 1-13.
- YUSUFF, A. S., BHONSLE, A. K., BANGWAL, D. P. & ATRAY, N. 2021. Development of a bariummodified zeolite catalyst for biodiesel production from waste frying oil: Process optimization by design of experiment. Renewable Energy, 177, 1253-1264.
- ZABETI, M., WAN DAUD, W. M. A. & AROUA, M. K. 2009. Activity of solid catalysts for biodiesel production: A review. Fuel Processing Technology, 90, 770-777.

**RESEARCH ARTICLE** 



## A Novel Water-Based Ink Varnish System for High-Speed Flexographic Paper Printing: Low Misting Colloid-Based Systems

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**Abstract:** In this study, ink misting performance and print resistance properties were obtained and were related to varying ink formulations using combinations of special acrylic emulsions, colloidal, and water-soluble resins. The misting and tackness performance of the two different colloids were investigated using an IGT TackOScope 3 SC. It was observed that acrylic colloids significantly affect the ink misting performance. After choosing the right colloidal resin and the optimum balance with the emulsion and water-soluble acrylic resin has yielded an excellent varnish that can be used in high-speed flexographic machines up to 700 m/min without misting. In industrial trials, 111,600 m of printing was carried out without misting and resolubility problems. In this paper, in addition to developing an ink that can run on high-speed machines, problems such as low print quality, resolubility, dry rub resistance, and tackness were solved and confirmed using industrial tests. From a sustainability perspective, process efficiency increased, and ink and paper waste minimized.

Keywords: water-based ink, printing ink, flexography, colloidal resin, misting, paper packaging.

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## 1. INTRODUCTION

Flexographic printing is a common printing technique in the packaging industry. This printing method is characterized primarily by the flexible printing plate and low viscosity inks, which allows it to be used on almost any surface (Johnson, 2008). Flexography has a number of advantages including high throughput, superior line edge definition, and reduced printing plate costs (Mariappan, Kim & Hart, 2020). Flexographic

printing, which uses molded rubber stamps to print graphics, is now turning into a nextgeneration electronics manufacturing technique for large-area displays and smart packaging at high speeds (Bhagya, Sunil, Shetty *et al.*, 2021).

Acrylic resins are the most successful of all waterborne technologies available and can be classified into four categories, which are alkali soluble resins, acrylic emulsions, colloidal emulsions and solutions and acrylic specialty
polymers. Colloidal emulsions are perfect for creating low-cost inks due to their high viscosity efficiency. Recent developments in colloidal emulsion technology have produced goods with outstanding print quality, superior economics for ink formulation, and the ability to disperse organic pigments (Laden, 1997). The water-soluble resin is used as the water-based ink's binder, and has a significant impact on the viscosity, adhesion, gloss, drying speed, printing adaptability, and preferred conditions (Mingzhi & Oluju, 2019).

The flexographic printing water-based varnish is simple to use, saves production costs, and is ideal for industrial use. Although solvent varnish has a long history of use, it can be toxic, irritating, and volatile, polluting the environment and putting the operator's health at risk. Water-based varnish is colorless, odorless, and free of organic volatiles, and it offers environmental protection, safety, low cost, and a diverse range of materials. Waterbased varnish is gradually replacing solvent-based varnish as a new green printing material. However, the current water-based varnish has a poor drying speed and is prone to process failures such as unstable product size (Ito & Suwa-Shi, 2018). However, today, the drying speed of waterbased resin systems have improved to perform similar drying as solvent-based inks on absorbent surfaces.

Flexographic printing water-based varnish can be prepared by adding a pure acrylic emulsion, a styrene-acrylic emulsion and auxiliary agents such as defoaming agents, waterborne wetting agents, wax additives, waterborne rheological aid, and other additives (Liu, Xie, Zhong, Fan & Qv, 2021). While stirring, a thickener and deionized water is also added to adjust the viscosity of the flexographic printing water-based varnish (Chen, 2011).

In water-based ink formulations, choosing the suitable mix of polymers is very important to obtain the desired properties. In the long print jobs, the resolubility property of the ink is required to obtain clean images. A resin solution can be added to the emulsion polymer in order to enhance resolubility. While choosing the acrylic emulsion resins, glass transition temperature (Tg) is a very important parameter. When the Tg is low, it provides better film formation, water resistance, flexibility, and adhesion, whereas, when the Tg is high, gloss, hardness, heat resistance, and drying speed will be better (Rentzhog & Fogden, 2006).

Jašúrek et. al tested the misting, which is the propensity of the ink splashing from the machine

rollers. This ink splashing can cause color contamination and servicing problems. Tack and misting of unemulsified inks and their emulsions were measured using the Kershaw Tackmaster-92. They found that, at the same temperature, unemulsified inks resulted in higher misting and bigger mist drops when compared to the emulsified inks (Jašúrek, Vališ, Syrový & Jablonovský, 2010).

The printing sector mostly generates paper and cardboard wastes, which are among the oldest and most widely used packaging materials. Most of these wastes can be recycled and used as secondary fibres in the manufacturing processes after being sorted, washed, and deinked. Ink is the second most waste-producing printing material. Ink wastes form during the post-printing phase, but solvent-based inks are also hazardous during the printing and post-printing phases due to the solvents they contain by evaporating and polluting the air. The safest ways to handle ink waste are either recycling the inks or burning the solvent they contain. A method for avoiding waste however, is to modify the manufacturing process to prevent waste, which can be accomplished by using water-based inks in production (Hayta & Oktay, 2019).

The average speed of the industrial bag printing machines in Turkey is almost half of the new generation printing machine speed, and high-speed technologies are just emerging. The technologies of the ink companies producing in Turkey are suitable for working at traditional printing machine operating conditions. At higher speeds such as 700 m/min, ink misting occurs which prevents efficient operation. Water-based varnish technology that can work at 700 m/min speed is not available in Turkey.

The aim of the study is to develop a water-based technology varnish that can efficiently work at high printing speed (700 m/min) with a continuous printing length of 10 reels/100,000 m, by providing an optimum ink transfer, drying speed, and preventing ink misting. Recently developed varnish systems will not only contain the quality features obtained in existing systems, but also prevent machine downtimes and ink contamination that affects print quality because of ink misting at high printing speed. In this way, printing companies might be able to increase their process efficiency, minimize ink and paper waste, and work time loss.

#### 2. MATERIALS AND METHODS

#### 2.1. Chemicals

The chemical names and the manufacturer names of the components used in this study are given in Table 1.

Table 1. (	Components	of water-based	technology	varnish.
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Ingredients	Manufacturer
Styrene Acrylic Emulsion Resin	BASF
Styrene Acrylic Emulsion Resin	BASF
Polyether Siloxane Emulsion Defoamer A	Evonik
Polyether Siloxane Defoamer B	Evonik
HDPE wax emulsion	Keim Additec
Ethylene diamine	Croda
Ammonia	Coldgaz
Monoethanolamine (MEA)	Ineos
Blue Color Base	Sun Chemical
Water	_

#### 2.2. Materials

The brown and white kraft sack papers used in this study were supplied by Mondi Group. The kraft sack paper, with an advantage speed of 90 g/m<sup>2</sup>, is an extensible high porosity paper combining high tensile energy absorption (TEA), excellent runnability, and very good printability. The main reason for choosing this paper was the paper features such as, a smooth paper surface, uniform paper formation, strength, and stiffness; and achieving a high-quality print result and allowing an effective operation of the high-speed machinery (Mondi Group, 2023).

#### 2.3. Experimental

For the preparation of the varnish samples, an acrylic solid resin was dissolved in water and MEA. Meanwhile, in a separate beaker, water, acrylic colloidal resin, ethylene diamine, and defoamer A and B were mixed at 3900 rpm for 5 min and then the ammonia and MEA were added slowly and mixed for 15 min to neutralize the colloidal resin. A solution of the acrylic resin, acrylic emulsion resin, and HDPE wax were added and mixed for 10 min as the final stage. Four different varnish samples (Sample A, Sample B, Sample C, and Sample D) were prepared by using different component combinations and amounts.

For the ink preparation, varnish, water, and blue color base were weighed in a beaker and stirred for 1 min for homogenization. Four ink samples were then prepared from each varnish sample.

Misting performance of the ink samples were compared using an IGT TackOScope 3 SC, at 350 m/min, at 20°C for 1 min, based on ASTM D 4361-97. Other tests were conducted using two samples with a low tendency to misting.

Ink samples were drawn down by depositing a layer of the ink and transferring to the surface of the substrate using the Harper QD Flexo Proofer, 200-lpc anilox.

Viscosity measurements of two samples were made with an ink viscosity in the range of 18 – 22 sec, under flexo printing conditions. Viscosity of the varnish and ink samples were measured with a DIN 53211-flow cup 4 mm, at 25°C. The optimum pH value of the water-based inks is between 8.2 – 9.5. The pH values were measured with a Mettler Toledo SevenCompact S220. The friction test result value must be greater than 4, so that the ink applied to the bags does not contaminate with friction during transportation and use. Rub resistance of the ink drawdowns were checked with a Sutherland 2000 rub tester with regards to ASTM D5264.

The friction coefficient value should be in the range of 0.2 - 0.3, in order to avoid slipping over each other and to prevent tipping during the transportation and storage of the printed bags. The Llovd LRX friction tester described in ISO 8295:1995 determined the kinetic coefficient of friction. The water resistance must be at the minimum level of four against the moisture that may come from the product placed in the bag and the effect of water that may accumulate on the surface of the bag from the outside environment. The water resistance of the printed samples was controlled according to DIN EN 646. The waterbased inks tend to foam during printing due to air pressure in the pneumatic pumps and the friction of the machine parts. The foaming tendency of the inks were tested by placing a 60 cc of sample into a beaker, stirring for 30 min at 3900 rpm, and then pouring the sample into 100 cc graduated

The other

cylinder immediately, checking the initial foam rise and foam level after 10 min, 20 min, and 30 min

#### **3. RESULTS AND DISCUSSION**

Initially, four different recipes were developed during the study and are shown in Table 2. In this

Sample C (g) Ingredients Sample A (g) Sample B (g) Sample D (g) Water 153.50 141.00 141.50 118.75 Surface active agent 2.50 2.50 2.50 2.50 37.50 Colloidal resin 1 43.75 43.75 Colloidal resin 2 62.50 Defoamer 1 0.25 0.25 0.25 1.25 Defoamer 2 1.00 1.00 1.00 1.25 6.25 4.00 4.00 3.50 Neutralization agent 37.50 43.75 37.50 Emulsion resin 25.00 Acrylic solution 12.50 12.50 12.50 12.50 Polyethylene wax 7.50 7.50 7.50 7.50 Total 250 250 250 250

Table 2. Details of the Recipe.

Since misting is one of the most important parameters, a comparative analysis of the recipes was carried out in terms of misting parameters using the IGT TackOScope 3 SC at 350 m/min, at 20°C for 1 min A4 size copy paper was then placed under the cylinders of the machine and at the end of the test, the ink stains were controlled on the paper. Results of the misting test were crucial to determine the final recipe. Figure 1 shows how much ink was splashed onto the A4 size copy paper. Sample A has the highest misting, followed by Sample C, the Reference sample, Sample B, and lastly Sample D. Based on these results, Sample A and Sample C were eliminated.

The tack tests of Sample B and Sample D were performed using the IGT TackOScope 3 SC at 50 m/min for 225 sec. According to the results shown in Figure 2, the Reference Sample and Sample D have similar tack profiles, whereas, Sample B has a lower tack profile. The maximum tack of the Reference Sample, Sample B and Sample D were measured as 80.39, 61.91, and 73.00 with the average tack of the samples measured as 40.34, 27.51, and 37.57 respectively. Since the emulsion resin amount is the same for Sample B and Sample D, it is seen that colloidal resin 1 has a lower tackness tendency than colloidal resin 2.

study, two different acrylic colloidal resins and two

ingredients are the same for all recipes, but the

amounts differ. Samples were prepared as 250 g for all recipes and several tests were performed.

different defoamers were used.

The foaming test was conducted as described in the experimental part of this study. The initial foam rise levels from 60 cc were observed as: 63 cc for the Reference Sample, 83 cc for Sample B, and 70 cc for Sample D. The recovery times to 60 cc were: 8 min for the Reference Sample, and 14 min for Sample B, and 12 min for Sample D. Recovery time, up to 25 min, generally does not cause problems while printing. However, longer than 25 min may cause printing problems especially when pneumatic pumps are used.

The coefficient of friction (COF) of the Reference Sample was 0.287, Sample B was 0.237, and Sample D was 0.278. The coefficient of friction is important for stacking printed bags. All samples have a convenient coefficient of friction that is in the range of 0.2 - 0.3. The friction coefficient value should be in the range of 0.2 - 0.3, in order to prevent slipping over each other on the stack.



Figure 1. Misting result of the inks.

The rub resistance test results are shown in Figure 3. The results are evaluated on a scale of one to five, one being for a bad rub resistance and five is for a perfect rub resistance. Since there is no ink stain on the blank substrate, the rub resistance of

the Reference Sample was evaluated as 4 and Sample B and Sample D as 5, respectively. A rub resistance value greater than 4 is convenient for the ink where it does not contaminate other surfaces during transportation and use.



Figure 2. Tackness curves of reference, Sample B and Sample D.



Figure 3. Rub resistance of Reference, Sample B and Sample D.

In a similar research about water-based flexographic ink with acrylic binders, Sonmez et. al found that the binder type influenced some print qualities, while the effect was not significant for others. One of the qualities that was not influenced by the acrylic type was the rub resistance (Sonmez, Alsaid, Pekarovicova *et al.*, 2023).

The first industrial print trial results of the Reference Sample, Sample B, and Sample D are shown in Figure 4. The printing machine speed

was 700 m/min and a 10,000 m length printed for each formulation. Sample D has the lowest misting, followed by Sample B and the Reference Sample. At the end of printing with the Reference Sample ink and Sample B ink, the accumulation of ink occurred in the hollow areas of the plate and formed residues in the form of droplets and dust, causing the design on the paper bag to become stained. Since Sample D, ink has the lowest misting, insignificant residues formed on the plate and the printed bag was not contaminated.



Figure 4. (a) Plate of the reference ink, (b) plate of the Sample B ink, (c) plate of the Sample D ink.

In the second industrial print trial, the machine speed was 700 m/min and the print length was

calculated at which the press stopped due to it reaching a level that could affect print quality.

Images of the clean photopolymer plate, dirty photopolymer plate after misting started and printed samples with the ink marks are shown in Figure 5. After the photopolymer plate shown in Figure 5(a) is used in the printing job, ink residues formed because of misting are collected in the hollow parts of the photopolymer plate as shown in Figure 5(b). When these formations accumulate more than the printing level of the photopolymer plate, they cause contamination in the final print. As seen in Figure 5(c), dot print impurities have formed in the white area that should be blank.



**Figure 5.** (Left) photopolymer plate before print, (middle) photopolymer plate after misting starts, (right) ink marks on the print after misting.

In Table 3, the approximate print length of the misting started, the total print length at which the print cannot be continued, and the number of printed reels are given. With the Reference Sample ink, 43,000 m printed; with Sample B ink, 75,000

m, and with Sample D ink 88,000 m printed without misting. Sample D has the highest total print length, whereas, the Reference Sample ink has the lowest.

Table 3. Industrial print trial results.

	Print length that ink misting started (m)	Total print length (m)	Number of printed reels
Reference	~43,000	62,000	5
Sample B	~75,000	99,200	8
Sample D	~88,000	111,600	9

The water resistance of the printed samples were tested in accordance with EN 646:2020 procedure C, short time contact. The test pieces were cut to a 50 mm x 20 mm dimension and the 60 mm x 90 mm glass fiber papers were immersed in deionized water. The glass fiber paper was then placed onto a 60 mm x 90 mm glass plate, and a test piece was put onto the fiber paper and covered with another glass fiber paper. A second glass plate

was covered on a second glass fiber paper and loaded with a mass of 1 kg for 10 min at  $(23 \pm 2)^{\circ}$ C. After 10 min, the glass fiber filter papers were checked to see whether there were any ink stains stained on them. The evaluation scale is from one to five, one is for too bad water resistance and five is for perfect water resistance. All of the samples were graded as 5 since there is no ink stain on the papers (Figure 6).



Figure 6. (a) Water resistance test results of the reference ink, (b) Sample B ink, (c) Sample D ink.

The wash up performances of the inks were tested after the application with an anilox roller side by side, allowing for 1-min drying. After 1 min, the anilox rollers were washed with water, and all of the inks were removed easily both on the anilox cylinder and rubber part (Figure 7). A good wash up performance is important for the cleaning of anilox rollers and plates on the printing machines. If the wash up of the ink is not good, it causes

clogging on the anilox rollers, and the amount of transferred ink is reduced.



**Figure 7.** Wash-up control results of the anilox rollers, (a) reference and (b) Sample B are on the lefthand side, (c) reference and (d) Sample D are on the right-hand side.

#### 3. CONCLUSION

In this work, a new generation of water-based technology varnish that can be run on high-speed printing machines, was designed using a combination of acrylic colloidal resin and acrylic emulsion resin. Sample B and Sample D showed low misting and Sample A and Sample C showed high misting, which was investigated using an IGT TackOScope 3 SC. In addition to the misting performance, the tests continued with the Sample B and D, whose tack level was close to the Reference Sample. In the foaming test, Sample B and D showed a higher foaming tendency than the Reference Sample, the foam disappeared below the 25 min recovery time. Sample B and Sample D showed good wash-up performance and did not cause any clogging on the rubbers and aniloxes rollers. The water resistance, rub resistance, and COF measurements were found to be similar to the Reference Sample. Two different industrial trials were made, one with a fixed print length and the second print length up to a high misting level. The accumulation on the photopolymer was controlled at the end of the first trial, Sample D showed minimal misting, while the Reference Sample and Sample B showed a similar misting tendency. The print length of the second trial was calculated, the Reference Sample ink was run for a 43,000 m print, and Sample B ink was run for a 75,000 m print. Sample D ink was run for an 88,000 m print without misting, in total 111,600 m was printed with minimal misting that did not affect the print quality. According to the results obtained from the tests, Sample D showed the best overall performance and it could be a guide to the design of inks to be used in machines capable of printing at speeds higher than 700 m/min in the future.

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#### **5. REFERENCES**

- Bhagya, R. S., Sunil, D., Shetty, P., Kagatikar, S., Wagle, S., Lewis, P. M., Kulkarni, S. D., & Kekuda, D. (2021). Water-based flexographic ink using chalcones exhibiting aggregation-induced enhanced emission for anti-counterfeit applications. Journal of Molecular Liquids, 344, 117974. https://doi.org/10.1016/j.molliq.2021.1179 74
- Chen, J. (2011). Flexographic printing water-based varnish and preparation method thereof (Eur. Pat. Appl. CN102102311A).
- Hayta, P., & Oktav, M. (2019). The importance of waste and environment management in printing industry. EJENS, 3(2), 18. https://dergipark.org.tr/en/download/article -file/826647
- Ito, H., & Suwa-Shi, N. (2018). Water-based ink composition for inkjet recording and coloring material liquid (Eur. Pat. Appl. EP3378907A1).
- Jašúrek, B., Vališ, J., Syrový, T., & Jablonovský, B. (2010). Study of rheological properties and tack of offset printing inks. Science & Technology, 18. https://www.scribd.com/document/6048699 28/ICJ-04-18-jasurek-valis-syrovyjablonovsky-2
- Johnson, J. (2008). Aspects of flexographic print quality and relationship to some printing parameters (Master's thesis). Karlstad University, Faculty of Technology and Science, Chemical Engineering. https://www.diva-portal.org/smash/get/diva 2:5784/FULLTEXT01.pdf
- Laden, P. (1997). Chemistry and technology of water-based inks (1st ed.). Blackie

Academic and Professional. https://www.waterstones.com/book/chemist ry-and-technology-of-water-based-inks/pladen/9789401071901

- Liu, Q., Xie, X., Zhong, Y., Fan, H., & Qv, X. (2021). Research on waterborne printing varnish and anti-adhesion. In Advances in Graphic Communication, Printing and Packaging Technology and Materials: Proceedings of 2020 11th
- China Academic Conference on Printing and Packaging (p. 614). https://doi.org/10.1007/978-981-16-0503-1\_88
- Mariappan, D. D., Kim, S., & Hart, A. J. (2020). A precision desktop plate-to-roll apparatus for development of advanced flexographic printing processes. Precision Engineering, 66, 392. https://doi.org/10.1016/j.precisioneng.2020 .07.012

- Mingzhi, J., & Qiuju, W. (2019). High-speed printing water-based ink (Eur. Pat. Appl. CN109181403A).
- Mondi Group. (2023, September 21). Sack Kraft paper. https://www.mondigroup.com/en/productsand-solutions/sack-kraft-paper/
- Rentzhog, M., & Fogden, A. (2006). Print quality and resistance for water-based flexography on polymer-coated boards: Dependence on ink formulation and substrate pretreatment. Progress in Organic Coatings, 57(3), 183. https://doi.org/10.1016/j.porgcoat.2006.08. 003
- Sonmez, S., Alsaid, D., Pekarovicova, A., Fleming, P. D. III, & Stoops, M. T. (2023). Effects on print quality of varying acrylic binder types in water-based flexographic ink formulations. Coloration Technology, 139(3), 330-337.



## Heterogeneous Catalysts for Biodiesel Production: Development of Bimetallic Catalysts Supported by Activated Carbon

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**Abstract**: This research, which explores the potential of activated carbon-supported co-impregnated metal catalysts, has the potential to significantly contribute to the field of energy systems engineering and the future of biodiesel production. In this study, spruce sawdust was used to produce activated carbon. A single-step method was applied for carbonization and activation. Spruce:KOH was adjusted as 1:2 and carbonized at 800 °C for 1 hour under nitrogen gas flow. The metal pairs were prepared with a 1:1 mass ratio for each metal. Then, 10% (w/w) metal pairs such as Cu-Fe, Fe-Zn, and Cu-Zn are impregnated on activated carbon. The catalysts were calcinated at 550 °C for 3 hours under a nitrogen atmosphere. Various characterization techniques, such as BET, SEM-EDS, and XRD analysis, were used to analyze the activity of these heterogeneous catalysts. The catalyst loading was 5% of the oil weight, the molar ratio of alcohol to oil was 19:1, the reaction temperature was 65 °C, and the reaction time was 3 hours in the esterification reaction of sunflower. According to the results, all metal pairs obtain similar FT-IR results. The biodiesel yields for Fe-Zn/AC, Cu-Zn/AC, and Cu-Fe/AC were calculated as 74.67%, 89.02%, and 68.16%, respectively.

Keywords: Biomass, biodiesel production, bimetallic catalyst, heterogeneous catalyst, activated carbon .

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#### **1. INTRODUCTION**

Due rapid population growth and to global energy industrialization, consumption increases daily, creating a critical energy crisis (Gupta & Rathod, 2019; Oyekunle et al., 2023a). Although fossil fuels now lead the energy industry, the trend towards biofuels is growing due to the depletion of fossil fuel sources and the adverse environmental effects (Karabulut et al., 2023; Monika et al., 2023; Thapa et al., 2018). On the other hand, the promotion of alternative energy sources has significantly increased over the past few decades due to growing political and societal awareness of environmental preservation and energy security. Governments, as key players in this transition, are actively promoting and investing in sustainable energy production by using biofuels instead of fossil fuels, providing reassurance and confidence in the future of energy (Chong et al., 2021; Kazıcı et al., 2021).

One of the most significant biofuels, and one whose significance is growing daily, is biodiesel (Asghari et al., 2022; Monika et al., 2023; Pacheco et al., 2022). Biodiesel is a cleaner-burning, less toxic alternative to petroleum diesel that can be used in diesel engines either in its pure form or blended with petroleum diesel (Du et al., 2018). Because of its greater flash point, biodiesel is more suited for handling and transportation. Moreover, compared to petroleum diesel, it has a better combustion emission profile with reduced emissions of carbon monoxide, particulate matter, and unburned hydrocarbons (Patle et al., 2014). Several techniques, such as micro-emulsion, pyrolysis, transesterification, and in-situ transesterification, can be used to produce biodiesel (Ahmed et al., 2023). Transesterification is the process of dispersing triglyceride and alcohol molecules, usually methanol, to replace the glycerol component with the alkyl group from the alcohol (Asghari et al., 2022). Animal fats and a

variety of vegetable oils can be used as raw materials (Li & Liang, 2017; Wahyono et al., 2022). One of the most critical factors for the transesterification reaction to proceed is catalyst addition. In the transesterification process, both homogeneous and heterogeneous catalysts are used. (Ahmed et al., 2023).

Typically, homogeneous catalysts used in oil transesterification include strong acids, strong bases, and free enzymes, such as KOH, NaOH, concentrated H₂SO₄, benzenesulfonic acid. CH<sub>3</sub>ONa, organic amines, and microbial lipases (Xie & Li, 2023). These catalysts were selected because of their catalytic efficiency and capacity to operate in mild conditions (Angulo et al., 2020; Atadashi et al., 2013). Disadvantages of the homogeneous catalyst include the difficulties in catalyst separation, soap formation, and the use of low-free fatty acid oil (Munyentwali et al., 2022). Due to their reusability, simplicity in separation from products, and high economic efficiency, the use of heterogeneous catalysts is increasing (Fonseca et al., 2019; Jayakumar et al., 2021; Onat, Ahmet Celik, et al., 2024). The process can be run continuously because heterogeneous catalysts are simple to remove, recycle, and regenerate from the reaction. Additionally, they reduce the waste materials disposed of, avoid separation issues, and prevent soap formation. Heterogeneous catalysts have a longer lifespan, are non-corrosive, and are favorable to the environment (Dahdah et al., 2020; Oyekunle et al., 2023a; Tshizanga et al., 2017). Additionally, heterogeneous catalysts had a higher tolerance of free-fatty acid ratio and water content in the oil (Mandari & Devarai, 2022). Heterogeneous catalysts also have some drawbacks compared to catalysts, including homogeneous lower selectivity, internal mass transfer limitations, more district operation parameters, faster deactivation, longer reaction time, and the existence of big grains of catalyst (Fonseca et al., 2019; Mbaraka & Shanks, 2006; Naeem et al., 2021; Oyekunle et al., 2023a; Pandya et al., 2022; Semwal et al., 2011). Therefore, it's critical to create a stable solid catalyst and increase the stability of active species. Furthermore, the kind of oil feedstock parameters used. operating the of transesterification process, and the catalyst's active site availability all affect a heterogeneous catalyst's efficiency. The important parameters, including catalyst loading ratio, the porosity of the catalyst, the specific surface area of the catalyst, dimensions and particle size of the catalyst, calcination temperature and time, reaction time and temperatures, blending ratio, and alcohol: oil molar ratios, have a main impact on the yield and quality of the biodiesel (Ekinci & Onat, 2024; Osman et al., 2023; Oyekunle et al., 2023b). Metal hydroxides, metal complexes, metal oxides, zeolites, hydrotalcite, and supported catalysts are types of heterogeneous catalysts (Demirci et al., 2023; Şahin et al., 2020; Semwal et al., 2011). In addition, supported material is important for

support materials offer a uniform dispersion across a greater surface area, even as they boost the stability of the catalysts. Between the support material and the active catalyst, there are adhesion contacts, van der Waals interactions, electron transfers, and distinct interphase surface structures (Hagen, 2005; Meşe et al., 2018; Onat, İzgi, et al., 2024). Support materials include a wide range of substances, including polymers, zeolites, graphene oxide, activated carbon, silica, and alumina (Abbas, 2023; Hoang et al., 2020; Onat et al., 2024; van Deelen et al., 2019). Szkudlarek et al. performed 5%Cu-1%Ru/BEA catalyst for biodiesel production. Reaction

heterogeneous catalysts. On the other hand, the

catalvst for Reaction temperature, reaction time, methanol:oil ratio, and catalyst loading were chosen as 220 °C, 2 h, 9:1, and 5%, respectively. The maximum biodiesel yield was 85.1% in these conditions (Szkudlarek et al., 2024). Farokhi and Saidi tried NiZnFe<sub>2</sub>O<sub>4</sub>, CoZnFe<sub>2</sub>O<sub>4</sub>, and CuZnFe<sub>2</sub>O<sub>4</sub> catalysts to produce biodiesel from neem oil. According to their results maximum biodiesel yields were found 99.29% for NiZnFe<sub>2</sub>O<sub>4</sub> catalyst (52.5 min, 16,5:1 methanol:oil ratio, 4% of catalyst loading, and 78 °C), 93% for CoZnFe<sub>2</sub>O<sub>4</sub> catalyst (61.7 min, 19,9:1 methanol:oil ratio, 4,5% of catalyst loading, and 78°C), and 90.86% for CuZnFe<sub>2</sub>O<sub>4</sub> catalysts (59.6 min, 21,7:1 methanol:oil ratio, 4,1% of catalyst loading, and 80°C) (Farokhi & Saidi, 2022). Kwong and Yung studied Ca and Fe catalysts for biodiesel production. The highest conversion yield was calculated as 99.5% for Ca/Fe catalyst at 1 hour reaction time, 120 °C, 20:1 of methanol:oil ratio, and 6% of catalyst loading (Kwong & Yung, 2015). Duan et al. used insect lipids to produce biodiesel. Ce-Cr/Zn catalyst was used in their study. The highest biodiesel conversion was found as 92.06% at 65 °C, 2.5% of catalyst loading, 10:1 of methanol to lipid ratio, and 8 hours of reaction time (Duan et al., 2024).

In this study, metal pairs, such as Cu-Fe, Cu-Zn, and Fe-Zn, were co-impregnated on activated carbon to produce biodiesel from sunflower oil. Sunflower oil, being an edible oil, offers consistent chemical composition and quality, which is essential for evaluating the catalytic performance of newly developed metallic catalysts. Waste oils often vary significantly in their composition due to and contaminants, degradation products, impurities, which could introduce variability and affect the interpretation of the catalytic performance. This work explores the development and use of co-impregnated metal catalysts supported by activated carbon for biodiesel synthesis, employing a novel combination of metal pairs and the supported material for the first time in the literature. The study uses activated carbon made from spruce sawdust, produced by a single carbonization and activation phase, as a support material for metal couples such as Cu-Fe, Fe-Zn, and Cu-Zn. In the esterification of sunflower oil, the study looks at these metal pairings' catalytic

effectiveness for particular reaction parameters, such as a 19:1 molar ratio of alcohol to oil, 65 °C temperature, and 5% catalyst loading. Biodiesel yields are utilized to gauge performance, and characterization methods, including BET, SEM-EDS, and XRD, are used to examine the catalysts' chemical and physical characteristics. The results of this study provide fresh information on the complementary effects of these co-impregnated metals, which are used in combination for the first time in the synthesis of biodiesel.

#### 2. EXPERIMENTAL SECTION

#### 2.1. Materials

Potassium hydroxide (KOH) and hydrochloric acid (HCl) were purchased from Merck, methanol (CH<sub>3</sub>OH) and zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) were purchased from Sigma-Aldrich, copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O) and iron(III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O) were purchased from Zag Chemicals. All chemicals were used directly without any further purification, except for the spruce-derived activated carbon, which was activated before use.

#### 2.2. Catalyst Preparation

Woody-based activated carbon was used as support material for bimetallic catalysts. Spruce wood sawdust was used as feedstock. Spruce sawdust was sieved through a 60-mesh screen (250 µm). The particles smaller than 60 mesh were used in the experiment. After sieving, spruce sawdust was dried in the oven at 104 °C for 24 h. KOH was used as an activation agent to prepare activated carbon. KOH was first dissolved in deionized water and mixed with spruce wood sawdust (2:1, weight ratio) for 24 hours and constant stirring. The mixture was then placed in an oven for 24 hours to remove the water. After drying, the mixture was subjected to calcination in a tubular furnace at 800 °C for 1 hour under nitrogen atmosphere to expand the pore size of the activated carbon. The heating rate was set as 10°C/min. After calcination in the tubular furnace, the activated carbon was washed with 0.5 M HCl to remove any residual KOH and then rinsed with deionized water until the pH reached 7. The cleaned activated carbon was then placed in an oven and dried for 24 hours. The activated support material in this study is called AC.

Co-impregnation method was used for catalyst synthesis.  $Zn(NO_3)_2.6H_2O$ ,  $Cu(NO_3)_2.3H_2O$ , and  $Fe(NO_3)_3.9H_2O$  were used, and the metal nitrate ratio was set as 50/50 (w/w) for each metal pair. First, two metal nitrates were dissolved in deionized water to a final concentration of 0.1 M. AC was added to this solution, with the metal nitrate to AC mass ratio set at 10%. The mixture was stirred with a magnetic stirrer for 24 hours at room temperature. Then, the solution was kept in an oven at 104 °C for 24 hours to evaporate the water. The dried catalyst was calcinated in a tubular furnace at 550 °C for 3 hours under

nitrogen atmosphere, with a heating rate of 10 °C/min. After calcination, three different bimetallic catalysts were obtained. These catalysts were named as Cu-Fe/AC, Cu-Zn/AC, and Fe-Zn/AC.

#### 2.3. Catalyst Characterization

To determine catalyst characterization, elemental analysis, Brunauer-Emmett-Teller (BET) analysis, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), Fourier Transform Infrared (FTIR), and X-Ray diffraction analysis (XRD) were applied. Dry sample composition was determined using an elemental analyzer (LECO CHNS-932, LECO, USA) to determine the contents of C, H, N, and S. The Quantachrome-Autosorb iQ BET analyzer (Anton Paar, Austria) was used to measure the surface area and pore structure properties of activated carbons at 77 K in the relative pressure range of 0.001 to 0.99. The samples were degassed at 180 °C for 24 hours prior to analysis. Fourier Transform Infrared (FTIR) spectra of catalysts were acquired by combining a universal attenuated total reflectance (ATR) sampling equipment with a diamond crystal with an FTIR analyzer (Perkin Elmer, USA). The 400-4000 cm<sup>-1</sup> region of the spectra was collected at a resolution of 4 cm<sup>-1</sup>. The surface morphologies of catalysts were examined using a scanning electron microscope (SEM) manufactured by Inspect S50 FEI Inc (USA). Using an X-ray diffractometer (Rigaku Smartlab, Japan) operating at 40 kV and 30 mA, with a scan range of 10 to 80 °C, a step width of 0.02 °C, and a scan speed of 3.035 °C/min, the X-ray diffraction (XRD) patterns of catalysts were obtained.

#### 2.4. Transesterification of Oil

The transesterification reaction of sunflower oil and methanol was carried out in a 500-mL, threeneck, round-bottom flask equipped with a reflux condenser. The catalyst dosage was 5% of the weight of the oil, and the molar ratio of the methanol to oil was 19:1. The reaction was carried out at 65°C for 180 minutes. After completion, the catalyst was separated by filtration. The remaining liquid product, containing biodiesel and glycerol, was transferred to a separatory funnel to separate the glycerol phase at the bottom. The upper layer, biodiesel, was then rinsed in a beaker and heated at 90 °C to remove residual methanol.

The biodiesel yield was calculated using the equation below.

% Yield =  $M_{\text{biodiesel}}/M_{\text{oil}} \times 100$ 

In this equation,  $M_{\text{biodiesel}}$  and  $M_{\text{oil}}$  were produced biodiesel and the weight of oil used in the experiment, respectively.

#### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of Catalysts

#### *3.1.1. Elemental Analysis*

Elemental analysis was done to find out the content of C, H, N, and S elements in the sample. The amount of oxygen in the sample is found by subtracting the total of C, H, N, and S obtained from the elemental analysis from 100. According to elemental analysis, the spruce sawdust includes 47.59% of C, 3.50% of H, 0.00% of N, 0.00% of S, and 47.51% of O. After activation and carbonization of spruce sawdust, AC includes 92.85% of C and 7.15% of O.

surface area of solid materials. This method can analyze a wide range of solid matrices, including catalyst powders and monolithic materials. BET analysis evaluates both the surface areas of catalysts and the dimensions of their pores. BET analysis was done in Autosorb iQ Station 1, the bath temperature is 77.35 K using 6 mm w/o rod cell type, with a relative pressure range of 0.001 and 0.99. It was performed after 12 hours of nitrogen desorption. The results, including the catalyst pore sizes, are detailed in Table 1.

#### 3.1.2. BET analysis

Based on gas adsorption measurements, BET theory can be used to calculate the specific

	Surface Area(m²/g)	Average pore Radius (Å)	Total pore volume (cm³/g)	Micropore volume (cm³/g)	Micropore area (m²/g)
AC	1231.97	955.24	588.40	0.47	1113.77
Cu-Fe/AC	1269.48	937.57	595.10	0.50	1165.72
Cu-Zn/AC	1191.00	935.25	556.90	0.47	1095.76
Fe-Zn/AC	1178.59	939.51	553.70	0.46	1081.00

The analyses showed that the surface area and pore diameter were similar. This outcome is expected, as both increases during the activated carbon production from spruce sawdust. Subsequent metal adsorption is not anticipated to alter the pore diameter significantly. Cu-Zn/AC and Fe-Zn/AC slightly decreased the surface area, while Cu-Fe/AC slightly increased. Im et al. tried Cu-Fe, Cu-Ni, and Cu-Co on  $Al_2O_3$  support, and the specific surface areas were found to be 141.3 m<sup>2</sup>/g, 136.1 m<sup>2</sup>/g, and 133.2 m<sup>2</sup>/g. The highest specific surface area was Cu-Fe/ $Al_2O_3$  (Im et al., 2024). Alotaibi made a green synthesis Cu-Zn/zeolite catalyst in their study. Adding Cu-Zn metals to the bare zeolite support's surface

significantly decreased the surface area from 252 to 165 m<sup>2</sup>/g (Alotaibi, 2023). One possible cause of the decreased BET surface area might be the metals that have been deposited, blocking the pores in the activated carbon or accumulating on the support surface (S. Wang et al., 2023).

#### *3.1.3. Scanning Electron Microscopy coupled with Energy Dispersion Spectroscopy (SEM-EDS) analysis*

SEM-EDS analysis observes the structure of catalysts and the metals attached to them. The EDS analysis of activated carbon without metal loading is shown below.



Figure 1: SEM-EDS analysis of AC.

Figure 1 shows the SEM-EDS analysis of activated carbon. No metal was detected as expected. Only carbon and oxygen content were considered. The

analysis showed that the activated carbon consists of 93% carbon and 7% oxygen.



Figure 2: SEM-EDS analysis of Cu-Fe/AC.



Figure 3: SEM-EDS analysis of Cu-Zn/AC.



Figure 4: SEM-EDS analysis of Fe-Zn/AC.

Table 2: EDS result of Cu-Fe/AC, Cu-Zn/AC, and Fe-Zn/AC catalyst.

Catalyst	Cu (%)	Zn (%)	Fe(%)	
Cu-Fe/AC	66.6		33.4	
Cu-Fe/AC	77.7		22.3	
Cu-Fe/AC	71.4		28.6	
Cu-Zn/AC	44.7	55.3		
Cu-Zn/AC	49.9	50.1		
Cu-Zn/AC	42.9	57.1		
Fe-Zn/AC		58.6	41.4	
Fe-Zn/AC		58.5	41.5	
Fe-Zn/AC		56.6	43.4	

Figures 2, 3, and 4 illustrate the average metal retention levels determined by the SEM-EDS method. The retention rates for the Cu-Fe/AC catalyst do not appear to be very balanced, with copper retention rates ranging from 66.6% to 77.7%. Meanwhile, iron retention ranges from 33.4% to 22.3%. Given that equal amounts of metal are loaded during catalyst production, the catalyst retains less iron relative to copper. SEM-EDS analysis of Cu-Zn/AC shows that the copperzinc retention ratio is more evenly distributed than the iron-copper retention rate. Copper retention ranges from approximately 50.1% to 57.1%, while zinc retention ranges from 49.9% to 42.9%. The graphs show that the smoother distribution is achieved by absorbing copper and zinc into activated carbon. The Fe-Zn/AC SEM-EDS analysis yielded consistent results. The zinc retention ranges between 56.6% and 58.6%, while iron retention ranges between 43.4% and 41.4%. These results indicate that activated carbon retains less iron than zinc and copper. Bimetallic catalysts cannot have homogeneous metal contents, which may be caused by the two metals' competing

adsorption during the adsorption impregnation process (Üçer et al., 2006).

SEM images present that activated carbon are irregular structures with high roughness and have visible holes and cracks, which increase specific surface area and pore volume (Bakather, 2024; Phiri et al., 2023). Dark and white sides explained the presence of the active sites in the catalyst (Q. Wang et al., 2023). When we compare the catalysts, the Cu-Fe/AC and Fe-Zn/AC catalysts show more cracks and holes, while the Cu-Zn/AC catalyst has less visible. This also explains why the surface area of the Cu-Zn/AC catalyst appears lower in the BET results.

#### 3.1.4. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) patterns of activated carbon were obtained using a Rigaku Smartlab X-ray diffractometer which operates at 40 kV and 30 mA. The device has a scanning range of 10 to 80°, a width of 0.02°, and a scanning speed of 3.035°/min.



a) SEM images of AC

b) SEM images of Cu-Fe/AC



c) SEM images of Cu-Zn/AC

d) SEM images of Fe-Zn/AC



Figure 6 presents the XRD results for both unloaded AC and metal pairs loaded ACs. Products made from activated carbon are mostly amorphous, while some crystalline material is The present. prominent XRD peaks at approximately 26° and 44° indicate an amorphous structure composed of simultaneously arranged, aromatic graphene-like sheets (Mallick et al., 2020; Mopoung & Dejang, 2021). Exhibited phases of CuO at 20 values of 32.7°, 35.8°, 38.9°, 46.1°, 48.9°, 53.4°, 58.7°, 61.3°, 66.4° and 68.0° (JCPDS card no. #45-0937) (Bienholz et al., 2010; Charate et al., 2021) and ZnO at 20 values of 31.9°, 34.1°,

36.7°, 47.7°, 56.5°, 62.4°, 66.59°, 68.3° and 68.92° (JCPDS card No. #36–1451) (Bel Hadj Tahar et al., 2008; Skuhrovcová et al., 2019). According to standard JCPDS card No. #22-1012, the diffraction peaks at 20 values of 29.95°, 35.30°, 36.98°, 42.82°, 53.21°, 56.64°, 62.27° and 73.63° can be present to a cubic phase of spinel ZnFe<sub>2</sub>O<sub>4</sub> (Iza et al., 2020). For CuFe<sub>2</sub>O<sub>4</sub>, the diffraction angles (20) 18.61, 30.17, 36.15, 39.01, 44.02, 54.22, and 62.39 complied with the characteristic data of JCPDS card no#034-0425 (Maleki et al., 2019).



Figure 6: XRD results of catalyst.

#### 3.2. Characterization of Biodiesel

3.2.1. FTIR results

The percentage of biodiesel in the sunflower oil transesterification reaction has been determined using the FTIR method. Samples were analyzed using Infrared mid-range in the region extending from 650-4000 cm<sup>-1</sup>, which covers the absorption bands characteristic of biodiesel (methyl ester) and sunflower oil (Foroutan et al., 2022; Santiago-Torres et al., 2014). FTIR results are shown in Figure 7.

At approximately  $330 \text{ cm}^{-1}$ , a wide vibration band declares that this structure includes O-H bonds that correspond to the presence of methanol (Santiago-Torres et al., 2014). The 3004, 2926, and 2853 cm<sup>-1</sup> peaks show carboxylic acid compounds. The firm ester peaks of FTIR are around 1745 cm<sup>-1</sup> (C=O bonds) and 1163-1281 cm<sup>-1</sup> (C-O bonds) (Lima et al., 2022; Onat & Ekinci, 2024).The

presence of these peaks confirms the occurrence of a transesterification reaction and biodiesel production. The peak at 1015 cm<sup>-1</sup>, which is not present in sunflower oil, also confirms biodiesel production from sunflower oil. The green line indicates the FTIR results of sunflower biodiesel from the KOH catalyst. The biodiesel production parameters are %3 of catalyst loading, 5:1 of methanol:oil ratio, 65 °C of reaction temperature, and 90 min of reaction time. The reaction parameters are standard biodiesel production from homogeneous basic catalysts. Biodiesel production from these four catalysts seems to be similar. This indicates that the quality of the produced biodiesel is consistent across all these catalysts and this shows that the biodiesels produced with metallic catalysts are very similar in bond structure to the biodiesels produced with homogeneous basic catalysts.



Figure 7: FTIR results of biodiesel from Cu-Fe/AC, Fe-Zn/AC, Cu-Zn/AC, and KOH catalysts.

#### 3.3. Yield of Biodiesel

Biodiesel conversion yields are determined based on the ratio of biodiesel to oil used. In this respect, the biodiesel conversion rates for Fe-Zn/AC, CuZn/AC, and Cu-Fe/AC were calculated at 74.67%, 89.02%, and 68.16%, respectively. The Cu-Zn metal pair achieves the highest conversion.

Table 3: Comparison of the biodiesel yield from sunflower oil with other literature studies.

Catalyst Type	Catalyst Ratio	Methanol:Oil Molar Ratio	Time (h)	Temp (°C)	Biodiesel Yield (%)	Reference
Ca-Mg-Al	2.5	15:1	6	60	95.00	(Dahdah et al., 2020)
CaO	3	13:1	1.66	60	94.00	(Granados et al., 2007)
$K_2CO_3$ /alumina-silica	2	15:1	0.33	120	97.00	(Lukić et al., 2009)
Waste chalk/CoFe₂O₄/K₂CO <sub>3</sub>	2.65	15.2	2.95	80	99.27	(Foroutan et al., 2022)
MgO-La <sub>2</sub> O <sub>3</sub>	3	18:1	5	60	97.70	(Feyzi et al., 2017)
CaO derived from sugar industry waste catalyst	5	15:1	2	60	87.64	(Bedir & Doğan, 2021)
Ca/Chicken eggshell	9	15:1	8	65	80.20	(Farooq et al., 2015)
Fe-Zn/AC	5	19:1	3	65	74.67	This study
Cu-Zn/AC	5	19:1	3	65	89.02	This study
Cu-Fe/AC	5	19:1	3	65	68.16	This study

The results show that the Cu-Zn/AC catalyst yields are consistent with literature values, whereas the other two are not. To improve conversion yields, different working conditions must be tested. As seen from the results of the SEM-EDS analysis of Cu-Zn/AC, a homogeneous distribution of the copper-zinc retention ratio and a more homogeneous structure compared to other

catalyst types effectively increased catalytic activity.

#### 4. CONCLUSION

As a result, this study produces biomass-derived activated carbon and loads it with metal pairs to use as biodiesel conversion catalysts. Cu, Zn, and Fe were used as metals. The innovative use of spruce sawdust-derived activated carbon as a support for metal pairs such as Cu-Fe, Fe-Zn, and Cu-Zn marks a novel contribution to the literature. The results indicate that while activated carbon formation increased the surface area and pore diameter, metal impregnation did not significantly impact these properties. SEM and EDS analysis show that the metal pair Cu-Zn has the best distribution over activated carbon. A notable observation is the low iron retention across the catalysts; Fe, when paired with Cu or Zn, is less effectively retained on the activated carbon than expected. This suggests an uneven distribution of metals in the activated carbon. The highest biodiesel conversion was achieved with the Cu-Zn metal pair, reaching 89.02%, due to the nearly uniform distribution of copper and zinc on the surface. In contrast, the Cu-Fe metal pair yielded the lowest conversion rate at 68.16%. Based on these results, the effectiveness of the metal pairs in biodiesel conversion can be ranked as Cu-Zn > Fe-Zn > Fe-Cu. Despite variations in conversion yields, the biodiesel content remains consistent, indicating that all catalysts are effective for biodiesel production.

#### **5. CONFLICT OF INTEREST**

The author declares that she has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### 7. REFERENCES

- Abbas, G. (2023). Metal organic framework supported surface modification of synthesized nickel/nickel oxide nanoparticles via controlled PEGylation for cytotoxicity profile against MCF-7 breast cancer cell lines via docking analysis. Journal of Molecular Structure, 1287, 135445. https://doi.org/https://doi.org/10.1016/j.molstru c.2023.135445
- Ahmed, M., Ahmad, K. A., Vo, D.-V. N., Yusuf, M., Haq, A., Abdullah, A., Aslam, M., Patle, D. S., Ahmad, Z., Ahmad, E., & Athar, M. (2023).
  Recent trends in sustainable biodiesel production using heterogeneous nanocatalysts:

Function of supports, promoters, synthesis techniques, reaction mechanism, and kinetics and thermodynamic studies. Energy Conversion and Management, 280, 116821. https://doi.org/https://doi.org/10.1016/j.enconm an.2023.116821

- Alotaibi, M. A. (2023). Liquid phase methanol synthesis by CO2 hydrogenation over Cu-Zn/Z catalysts: Influence of Cd promotion. Journal of the Taiwan Institute of Chemical Engineers, 153, 105210. https://doi.org/https://doi.org/10.1016/j.jtice.202 3.105210
- Angulo, B., Fraile, J. M., Gil, L., & Herrerías, C. I. (2020). Comparison of Chemical and Enzymatic Methods for the Transesterification of Waste Fish Oil Fatty Ethyl Esters with Different Alcohols. ACS Omega, 5(3), 1479–1487. https://doi.org/10.1021/acsomega.9b03147
- Asghari, M., Hosseinzadeh Samani, B., & Ebrahimi, R. (2022). Review on non-thermal plasma technology for biodiesel production: Mechanisms, reactors configuration, hybrid reactors. Energy Conversion and Management, 258, 115514. https://doi.org/https://doi.org/10.1016/j.enconm an.2022.115514
- Atadashi, I. M., Aroua, M. K., Abdul Aziz, A. R., & Sulaiman, N. M. N. (2013). The effects of catalysts in biodiesel production: A review. Journal of Industrial and Engineering Chemistry, 19(1), 14-26. https://doi.org/https://doi.org/10.1016/j.jiec.201 2.07.009
- Bakather, O. Y. (2024). Eco-friendly biosorbent for lead removal: Activated carbon produced from grape wood. Desalination and Water Treatment, 317, 100210.
  https://doi.org/https://doi.org/10.1016/j.dwt.202 4.100210
- Bedir, Ö., & Doğan, T. H. (2021). Use of sugar industry waste catalyst for biodiesel production. Fuel, 286, 119476. https://doi.org/https://doi.org/10.1016/j.fuel.202 0.119476
- Bel Hadj Tahar, N., Bel Hadj Tahar, R., Ben Salah, A., & Savall, A. (2008). Effects of Individual Layer Thickness on the Microstructure and Optoelectronic Properties of Sol-Gel-Derived Zinc Oxide Thin Films. Journal of the American Ceramic Society, 91(3), 846-851. https://doi.org/https://doi.org/10.1111/j.1551-2916.2007.02221.x
- Bienholz, A., Schwab, F., & Claus, P. (2010). Hydrogenolysis of glycerol over a highly active

CuO/ZnO catalyst prepared by an oxalate gel method: influence of solvent and reaction temperature on catalyst deactivation. Green Chemistry, 12(2), 290–295. https://doi.org/10.1039/B914523K

Charate, S., Shinde, S., Kondawar, S., Desai, U., Wadgaonkar, P., & Rode, C. (2021). Role of preparation parameters of Cu-Zn mixed oxide catalyst in solvent free glycerol carbonylation with urea. Journal of the Indian Chemical Society, 98(7), 100090. https://doi.org/https://doi.org/10.1016/j.jics.202 1.100090

Chong, C. T., Loe, T. Y., Wong, K. Y., Ashokkumar, V., Lam, S. S., Chong, W. T., Borrion, A., Tian, B., & Ng, J.-H. (2021). Biodiesel sustainability: The global impact of potential biodiesel production on the energy-water-food (EWF) nexus. Environmental Technology & Innovation, 22, 101408. https://doi.org/https://doi.org/10.1016/j.eti.2021 .101408

Dahdah, E., Estephane, J., Haydar, R., Youssef, Y., El Khoury, B., Gennequin, C., Aboukaïs, A., Abi-Aad, E., & Aouad, S. (2020). Biodiesel production from refined sunflower oil over Ca-Mg-Al catalysts: Effect of the composition and the thermal treatment. Renewable Energy, 146, 1242–1248. https://doi.org/https://doi.org/10.1016/j.renene. 2019.06.171

Demirci, S., Bektaş, H., Onat, E., Şahin, Ö., Baytar, O., & İzgi, M. S. (2023). Aktif karbon destekli ucuz ve kullanışlı katalizörün amonyak bor hidrolizinde incelenmesi. Journal of Boron, 8(2), 59–65. https://doi.org/10.30728/boron.1179156

Du, E., Cai, L., Huang, K., Tang, H., Xu, X., & Tao, R. (2018). Reducing viscosity to promote biodiesel for energy security and improve combustion efficiency. Fuel, 211, 194–196. https://doi.org/https://doi.org/10.1016/j.fuel.201 7.09.055

Duan, X., Yan, S., Tie, X., Lei, X., Liu, Z., Ma, Z., Wang, T., & Feng, W. (2024). Bimetallic Ce-Cr doped metal-organic frameworks as a heterogeneous catalyst for highly efficient biodiesel production from insect lipids. Renewable Energy, 224, 120128. https://doi.org/https://doi.org/10.1016/j.renene. 2024.120128

Ekinci, S., & Onat, E. (2024). Activated carbon assisted cobalt catalyst for hydrogen production: synthesis and characterization. Balıkesir Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 26(2), 455–471. https://doi.org/10.25092/baunfbed.1297146 Farokhi, G., & Saidi, M. (2022). Catalytic activity of bimetallic spinel magnetic catalysts (NiZnFe2O4, CoZnFe2O4 and CuZnFe2O4) in biodiesel production process from neem oil: Process evaluation and optimization. Chemical Engineering and Processing - Process Intensification, 181, 109170. https://doi.org/https://doi.org/10.1016/j.cep.202 2.109170

Farooq, M., Ramli, A., & Naeem, A. (2015). Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones. Renewable Energy, 76, 362–368. https://doi.org/https://doi.org/10.1016/j.renene. 2014.11.042

Feyzi, M., Hosseini, N., Yaghobi, N., & Ezzati, R. (2017). Preparation, characterization, kinetic and thermodynamic studies of MgO-La2O3 nanocatalysts for biodiesel production from sunflower oil. Chemical Physics Letters, 677, 19–29. https://doi.org/https://doi.org/10.1016/j.cplett.2 017.03.014

Fonseca, J. M., Teleken, J. G., de Cinque Almeida, V., & da Silva, C. (2019). Biodiesel from waste frying oils: Methods of production and purification. Energy Conversion and Management, 184, 205-218. https://doi.org/https://doi.org/10.1016/j.enconm an.2019.01.061

Foroutan, R., Peighambardoust, S. J., Mohammadi, R., Peighambardoust, S. H., & Ramavandi, B. (2022). Application of waste chalk/CoFe2O4/K2CO3 composite as a reclaimable catalyst for biodiesel generation from sunflower oil. Chemosphere, 289, 133226. https://doi.org/https://doi.org/10.1016/j.chemos phere.2021.133226

Granados, M. L., Poves, M. D. Z., Alonso, D. M., Mariscal, R., Galisteo, F. C., Moreno-Tost, R., Santamaría, J., & Fierro, J. L. G. (2007). Biodiesel from sunflower oil by using activated calcium oxide. Applied Catalysis B: Environmental, 73(3), 317–326. https://doi.org/https://doi.org/10.1016/j.apcatb. 2006.12.017

- Gupta, A. R., & Rathod, V. K. (2019). Solar radiation as a renewable energy source for the biodiesel production by esterification of palm fatty acid distillate. Energy, 182, 795–801. https://doi.org/https://doi.org/10.1016/j.energy. 2019.05.189
- Hagen, J. (2005). Industrial Catalysis. Wiley. https://doi.org/10.1002/3527607684

Hoang, V. C., Dinh, K. N., & Gomes, V. G. (2020).
Hybrid Ni/NiO composite with N-doped activated carbon from waste cauliflower leaves: A sustainable bifunctional electrocatalyst for efficient water splitting. Carbon, 157, 515–524.
https://doi.org/https://doi.org/10.1016/j.carbon. 2019.09.080

Im, Y., Muroyama, H., Matsui, T., Eguchi, K., Kim, Y., & Chae, H. (2024). Multifunctional effect of copper in bimetallic Cu-M/Al2O3 catalysts (M = Fe, Co, and Ni) for NH3 decomposition. Applied Surface Science, 669, 160396. https://doi.org/https://doi.org/10.1016/j.apsusc. 2024.160396

Iza, A. M., Primadi, T. R., Ciptawati, E., Sumari, Aliyatulmuna, A., Nazriati, Suryadharma, I. B., & Fajaroh, F. (2020). Synthesis of zinc ferrite (ZnFe2O4) using microwave assisted coprecipitation method and its effectivity toward photodegradation of malachite green. AIP Conference Proceedings, 2251(1), 040025. https://doi.org/10.1063/5.0015871

Jayakumar, M., Karmegam, N., Gundupalli, M. P., Bizuneh Gebeyehu, K., Tessema Asfaw, B., Chang, S. W., Ravindran, B., & Kumar Awasthi, M. (2021). Heterogeneous base catalysts: Synthesis and application for biodiesel production – A review. Bioresource Technology, 331, 125054. https://doi.org/https://doi.org/10.1016/j.biortech .2021.125054

Karabulut, A., İzgi, M. S., Demir, H., Şahin, Ö., & Horoz, S. (2023). Optimizing hydrogen production from alkali hydrides using supported metal catalysts. Ionics, 29(5), 1975–1982. https://doi.org/10.1007/s11581-023-04962-8

Kazıcı, H. Ç., İzgi, M. S., & Şahin, Ö. (2021). A comprehensive study on the synthesis, characterization and mathematical modeling of nanostructured Co-based catalysts using different support materials for AB hydrolysis. Chemical Papers, 75(6), 2713–2725. https://doi.org/10.1007/s11696-021-01514-0

Kwong, T.-L., & Yung, K.-F. (2015). Heterogeneous alkaline earth metal-transition metal bimetallic catalysts for synthesis of biodiesel from low grade unrefined feedstock. RSC Advances, 5(102), 83748-83756. https://doi.org/10.1039/C5RA13819A

Li, J., & Liang, X. (2017). Magnetic solid acid catalyst for biodiesel synthesis from waste oil. Energy Conversion and Management, 141, 126– 132. https://doi.org/https://doi.org/10.1016/j.enconm an.2016.06.072 Lima, A. C., Hachemane, K., Ribeiro, A. E., Queiroz, A., Gomes, M. C. S., & Brito, P. (2022).
Evaluation and kinetic study of alkaline ionic liquid for biodiesel production through transesterification of sunflower oil. Fuel, 324, 124586.
https://doi.org/https://doi.org/10.1016/j.fuel.202 2.124586

Lukić, I., Krstić, J., Jovanović, D., & Skala, D. (2009). Alumina/silica supported K2CO3 as a catalyst for biodiesel synthesis from sunflower oil. Bioresource Technology, 100(20), 4690–4696. https://doi.org/https://doi.org/10.1016/j.biortech .2009.04.057

Maleki, A., Hajizadeh, Z., & Salehi, P. (2019). Mesoporous halloysite nanotubes modified by CuFe2O4 spinel ferrite nanoparticles and study of its application as a novel and efficient heterogeneous catalyst in the synthesis of pyrazolopyridine derivatives. Scientific Reports, 9(1), 5552. https://doi.org/10.1038/s41598-019-42126-9

Mallick, A., Mukhopadhyay, M., & Ash, S. (2020). Synthesis, Characterization and Performance Evaluation of a Solid Acid Catalyst Prepared from Coconut Shell for Hydrolyzing Pretreated Acacia nilotica Heartwood. Journal of The Institution of Engineers (India): Series E, 101(1), 69–76. https://doi.org/10.1007/s40034-019-00153-1

Mandari, V., & Devarai, S. K. (2022). Biodiesel Production Using Homogeneous, Heterogeneous, and Enzyme Catalysts via Transesterification and Esterification Reactions: a Critical Review. BioEnergy Research, 15(2), 935–961. https://doi.org/10.1007/s12155-021-10333-w

Mbaraka, I. K., & Shanks, B. H. (2006). Conversion of oils and fats using advanced mesoporous heterogeneous catalysts. JAOCS, Journal of the American Oil Chemists' Society, 83(2), 79–91. https://doi.org/10.1007/s11746-006-1179-x

Meşe, E., Kantürk Figen, A., Coşkuner Filiz, B., & Pişkin, S. (2018). Cobalt-boron loaded thermal activated Turkish sepiolite composites (Co-B@tSe) as a catalyst for hydrogen delivery. Applied Clay Science, 153, 95–106. https://doi.org/https://doi.org/10.1016/j.clay.201 7.12.008

Monika, Banga, S., & Pathak, V. V. (2023). Biodiesel production from waste cooking oil: A comprehensive review on the application of heterogenous catalysts. Energy Nexus, 10, 100209.

https://doi.org/https://doi.org/10.1016/j.nexus.2 023.100209

Mopoung, S., & Dejang, N. (2021). Activated carbon preparation from eucalyptus wood chips using continuous carbonization-steam activation process in a batch intermittent rotary kiln. Scientific Reports, 11(1), 13948. https://doi.org/10.1038/s41598-021-93249-x

Munyentwali, A., Li, H., & Yang, Q. (2022). Review of advances in bifunctional solid acid/base catalysts for sustainable biodiesel production. Applied Catalysis A: General, 633, 118525. https://doi.org/https://doi.org/10.1016/j.apcata. 2022.118525

Naeem, M. M., Al-Sakkari, E. G., Boffito, D. C., Gadalla, M. A., & Ashour, F. H. (2021). One-pot conversion of highly acidic waste cooking oil into biodiesel over a novel bio-based bifunctional catalyst. Fuel, 283, 118914. https://doi.org/https://doi.org/10.1016/j.fuel.202 0.118914

Onat, E., Ahmet Celik, F., Şahin, Ö., Karabulut, E., & iZGİ, M. S. (2024). H2 production from ammonia borane hydrolysis with catalyst effect of Titriplex® III carbon quantum dots supported by ruthenium under different reactant Conditions: Experimental study and predictions with molecular modelling. Chemical Engineering Journal, 497, 154593. https://doi.org/https://doi.org/10.1016/j.cej.2024 .154593

Onat, E., & Ekinci, S. (2024). A new material fabricated by the combination of natural mineral perlite and graphene oxide: Synthesis, characterization, and methylene blue removal. Diamond and Related Materials, 143, 110848. https://doi.org/https://doi.org/10.1016/j.diamon d.2024.110848

Onat, E., Izgi, M. S., Şahin, Ö., & Saka, C. (2024). Nickel/nickel oxide nanocomposite particles dispersed on carbon quantum dot from caffeine for hydrogen release by sodium borohydride hydrolysis: Performance and mechanism. Diamond and Related Materials, 141, 110704. https://doi.org/https://doi.org/10.1016/j.diamon d.2023.110704

Osman, A. I., Elgarahy, A. M., Eltaweil, A. S., Abd El-Monaem, E. M., El-Aqapa, H. G., Park, Y., Hwang, Y., Ayati, A., Farghali, M., Ihara, I., Al-Muhtaseb, A. H., Rooney, D. W., Yap, P.-S., & Sillanpää, M. (2023). Biofuel production, hydrogen production and water remediation by photocatalysis, biocatalysis and electrocatalysis. Environmental Chemistry Letters, 21(3), 1315–1379. https://doi.org/10.1007/s10311-023-01581-7 Oyekunle, D. T., Barasa, M., Gendy, E. A., & Tiong, S. K. (2023a). Heterogeneous catalytic transesterification for biodiesel production: Feedstock properties, catalysts and process parameters. Process Safety and Environmental Protection, 177, 844–867. https://doi.org/https://doi.org/10.1016/j.psep.20 23.07.064

Oyekunle, D. T., Barasa, M., Gendy, E. A., & Tiong, S. K. (2023b). Heterogeneous catalytic transesterification for biodiesel production: Feedstock properties, catalysts and process parameters. Process Safety and Environmental Protection, 177, 844–867. https://doi.org/https://doi.org/10.1016/j.psep.20 23.07.064

Pacheco, J. R., Villardi, H. G. D., Cavalcante, R. M., & Young, A. F. (2022). Biodiesel production through non-conventional supercritical routes: Process simulation and technical evaluation. Energy Conversion and Management, 251, 114998. https://doi.org/https://doi.org/10.1016/j.enconm an.2021.114998

Pandya, H. N., Parikh, S. P., & Shah, M. (2022). Comprehensive review on application of various nanoparticles for the production of biodiesel. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 44(1), 1945–1958. https://doi.org/10.1080/15567036.2019.164859 9

Patle, D. S., Sharma, S., Ahmad, Z., & Rangaiah, G. P. (2014). Multi-objective optimization of two alkali catalyzed processes for biodiesel from waste cooking oil. Energy Conversion and Management, 85, 361–372. https://doi.org/https://doi.org/10.1016/j.enconm an.2014.05.034

Phiri, J., Ahadian, H., Sandberg, M., Granström, K., & Maloney, T. (2023). The Influence of Physical Mixing and Impregnation on the Physicochemical Properties of Pine Wood Activated Carbon Produced by One-Step ZnCl2 Activation. Micromachines, 14(3), 572. https://doi.org/10.3390/mi14030572

Şahin, Ö., Bozkurt, A., Yayla, M., Kazıcı, H. Ç., & İzgi, M. S. (2020). As a highly efficient reduced graphene oxide-supported ternary catalysts for the fast hydrogen release from NaBH4. Graphene Technology, 5(3), 103–111. https://doi.org/10.1007/s41127-020-00036-y

Santiago-Torres, N., Romero-Ibarra, I. C., & Pfeiffer, H. (2014). Sodium zirconate (Na2ZrO3) as a catalyst in a soybean oil transesterification reaction for biodiesel production. Fuel

Processing Technology, 120, 34–39. https://doi.org/https://doi.org/10.1016/j.fuproc.2 013.11.018

Semwal, S., Arora, A. K., Badoni, R. P., & Tuli, D. K. (2011). Biodiesel production using heterogeneous catalysts. Bioresource Technology, 102(3), 2151–2161. https://doi.org/https://doi.org/10.1016/j.biortech .2010.10.080

Skuhrovcová, L., Kolena, J., Tišler, Z., & Kocík, J. (2019). Cu–Zn–Al mixed oxides as catalysts for the hydrogenolysis of glycerol to 1,2propanediol. Reaction Kinetics, Mechanisms and Catalysis, 127(1), 241–257. https://doi.org/10.1007/s11144-019-01560-6

Szkudlarek, Ł., Chałupka-Śpiewak, K., Maniukiewicz, W., Albińska, J., Szynkowska-Jóźwik, M. I., & Mierczyński, P. (2024). Biodiesel Production via Transesterification Reaction over Mono- and Bimetallic Copper-Noble Metal (Pt, Ru) Catalysts Supported on BEA Zeolite. Catalysts, 14(4), 260. https://doi.org/10.3390/catal14040260

Thapa, S., Indrawan, N., & Bhoi, P. R. (2018). An overview on fuel properties and prospects of Jatropha biodiesel as fuel for engines.
Environmental Technology & Innovation, 9, 210–219.
https://doi.org/https://doi.org/10.1016/j.eti.2017.12.003

Tshizanga, N., Aransiola, E. F., & Oyekola, O. (2017). Optimisation of biodiesel production from waste vegetable oil and eggshell ash. South African Journal of Chemical Engineering, 23, 145–156. https://doi.org/https://doi.org/10.1016/j.sajce.20

17.05.003

Üçer, A., Uyanik, A., & Aygün, Ş. F. (2006). Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilised activated carbon. Separation and Purification Technology, 47(3), 113–118. https://doi.org/https://doi.org/10.1016/j.seppur. 2005.06.012

van Deelen, T. W., Hernández Mejía, C., & de Jong, K. P. (2019). Control of metal-support interactions in heterogeneous catalysts to enhance activity and selectivity. Nature Catalysis, 2(11), 955–970. https://doi.org/10.1038/s41929-019-0364-x

Wahyono, Y., Hadiyanto, H., Gheewala, S. H., Budihardjo, M. A., & Adiansyah, J. S. (2022).
Evaluating the environmental impacts of the multi-feedstock biodiesel production process in Indonesia using life cycle assessment (LCA).
Energy Conversion and Management, 266, 115832.
https://doi.org/https://doi.org/10.1016/j.enconm an.2022.115832

Wang, Q., Wang, C., Du, X., & Zhang, X. (2023). Controlled synthesis of M (M = Cr, Cu, Zn and Fe)-NiCoP hybrid materials as environmentally friendly catalyst for seawater splitting. Journal of Alloys and Compounds, 966, 171516. https://doi.org/https://doi.org/10.1016/j.jallcom. 2023.171516

Wang, S., Yang, J., Wang, S., Zhao, N., & Xiao, F. (2023). Effect of Cu and Zn on the performance of Cu-Mn-Zn/ZrO2 catalysts for CO2 hydrogenation to methanol. Fuel Processing Technology, 247, 107789. https://doi.org/https://doi.org/10.1016/j.fuproc.2 023.107789

Xie, W., & Li, J. (2023). Magnetic solid catalysts for sustainable and cleaner biodiesel production: A comprehensive review. Renewable and Sustainable Energy Reviews, 171, 113017. https://doi.org/https://doi.org/10.1016/j.rser.202 2.113017

**RESEARCH ARTICLE** 



### Potential of Waste Toner Powder for Sustainable Energy Production: An Assessment of Its Suitability for Bio-Briguette Applications

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Abstract: This study investigates the feasibility of utilizing waste toner powder (WTP) in the energy sector, focusing on its application in bio-briquette production. The research comprised two main phases: the characterization of WTP's structural, morphological, and fuel properties, followed by an evaluation of its potential as a biofuel component in direct combustion processes. WTP samples were collected from a recycling facility specifically established for toner cartridge recycling in the Elazığ Organized Industrial Zone. These samples were stored under appropriate conditions and analyzed using advanced techniques. The structural and morphological properties were examined using FTIR, SEM-EDX, and particle size distribution analyses. Particle size measurements revealed average diameters of 182.6 nm in toluene and 308.4 nm in benzene, with toluene providing a narrower and more uniform distribution. Fuel properties were assessed through proximate and ultimate analyses. The results indicated that WTP contains 88.38% volatile matter, 4.91% ash, and 2.67% moisture, with a higher heating value (HHV) of 35.56 MJ/kg. The ultimate analysis highlighted a significant carbon content (32.12%) and low nitrogen levels (1.98%), reinforcing its potential as a fuel. WTP's dispersion behavior was also evaluated in both media, confirming better stability in toluene. These findings demonstrate that WTP possesses favorable fuel properties, such as a high calorific value and strong binding capabilities, making it a promising raw material for bio-briquette production when mixed with powdered biomass waste sources like furniture factory waste. Producing biofuel pellets with WTP could enhance energy efficiency, reduce emissions, and improve transport and storage convenience. Utilizing WTP as an energy source not only provides a high-value solution for waste management but also supports environmental sustainability and landfill preservation.

**Keywords:** Waste Toner Powder, Bio-briquette, E-Waste Recycling, Energy Recovery, Sustainable Fuel Development.

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#### **1. INTRODUCTION**

The demand for electrical and electronic equipment (EEE) has been rapidly increasing due to urbanization, industrialization, and population growth. Devices such as refrigerators, air conditioners, computers, printers, and cartridges have become integral to daily life and play a significant role in the global economy (Cui and Forssberg, 2003). However, the widespread use of EEEs has led to a surge in e-waste, which contains both environmentally harmful and valuable components (Nnorom et al., 2008).

In 2003, Western Europe generated 6 million tons (Mt) of e-waste, while over 315 million computers in the United States reached the end of their service life in 2004. By 2006, global e-waste production had risen to 20–50 Mt annually, with most contributions from Europe, the United States, and Australia. In the coming years, emerging economies such as China, Eastern Europe, and Latin America are expected to become major e-

waste producers (Robinson, 2009). Despite these trends, e-waste was recognized as a significant issue only in 2008, when China implemented the "Waste Electrical and Electronic Equipment Recycling Management Regulation" to address this growing challenge.

Global e-waste production has risen by 9.2 Mt since 2014 and is projected to reach 74.7 Mt by 2030, nearly doubling within 16 years. In 2019, Asia led global e-waste generation with 24.9 Mt, followed by the Americas (13.1 Mt) and Europe (12 Mt), while Africa and Oceania produced 2.9 Mt and 0.7 Mt, respectively. On a per capita basis, Europe topped the list with 16.2 kg per person, trailed by Oceania (16.1 kg) and the Americas (13.3 kg), whereas Asia and Africa lagged significantly at 5.6 kg and 2.5 kg per person, respectively (Forti et al., 2020). The surge in e-waste is driven by increased EEE consumption, shorter product lifecycles, and limited repair options. Recycling and reuse are widely acknowledged as the most effective strategies for managing e-waste. However, in 2019, only 9.3 Mt (17.4%) of e-waste was officially documented as collected and recycled, underscoring the inability of recycling efforts to match the pace of e-waste generation (Forti et al., 2020). While the number of countries adopting ewaste policies has grown from 61 in 2014 to 78, progress in regulation and enforcement remains inconsistent, hindered by limited investment and political will. Consequently, initiatives to improve the collection and recycling of EEE waste are critical at both national and international levels (Devin et al., 2014). Additionally, ongoing research is exploring innovative ways to convert e-waste into high-value-added products (Gaikwad et al., 2018).

Despite efforts by the Chinese government to refill, renew, and remanufacture used toner cartridges under the "Waste Electrical and Electronic Equipment Recycling Management Regulation" enacted in 2008, the global number of discarded toner cartridges has continued to rise. Over the past two decades, even with advancements in digital communication and electronic document management systems, printers and cartridges remain significant sources of e-waste. Globally, approximately 375 million cartridges are added to e-waste annually-equating to around one million cartridges per day. Toner cartridges, composed of 35% low-cost HIPS (High-impact polystyrene) plastic, 39% iron, 8% toner powder, 13% aluminum, and 5% other materials, are largely recyclable and reusable. However, their limited lifespan, resistance to degradation in landfills, and challenges in recycling make them a substantial environmental concern. Improper disposal can result in soil and water pollution, posing significant health risks (Babar et al., 2019). Given their increasing contribution to global e-waste and the environmental hazards they pose, developing sustainable technologies for recycling and reusing

waste toner cartridges is critical. This necessity highlights the importance of addressing toner cartridge waste as part of broader e-waste management efforts.

In recent years, international efforts have focused reclaiming waste toner cartridges and on processing solid waste. Studies consistently highlight that landfilling and direct incineration are unsuitable disposal methods for toner cartridges due to several factors: (I) Plastics made from engineering-grade polymers degrade extremely slowly in the environment. (II) Incineration releases toxic gases, such as furans and dioxins, posing severe environmental and health risks. (III) Residual toner can leak during storage or incineration, contaminating the environment. As a result, mechanical recycling methods are widely regarded as the preferred approach for managing e-waste, including toner cartridges, as they minimize secondary pollution during the recovery process (Li et al., 2007; Wu et al., 2008; Veit et al., 2006; Park et al., 2009).

To determine the appropriate storage conditions for waste toner powder and facilitate its conversion into high-value-added products, it is essential to first categorize different cartridge types—inkjet, laser, and duplicator cartridges—and analyze their basic components.

Inkjet Printers: These use inks containing harmful chemicals such as butyl urea, cyclohexanone, ethoxylated acetylenic diols, ethylene glycol, and various sulfur-based dyes. The printing process releases volatile organic solvents, contributing to environmental pollution (Aydemir et al., 2020). Home inkjet printers typically require frequent replacement of cartridges (black, cyan, magenta, and yellow), leading to significant waste generation.

Laser Printers and Copiers: These rely on dry or wet toner formulations. Dry toners are primarily composed of acrylic and styrene powders mixed with pigments, while liquid toners use acrylic resins with added dyes for vibrant colors. Plastic resins, often comprising 45-90% of toner powder, are typically made from styrene and acrylic polymers (Vucinic et al., 2013). Additionally, certain toners contain iron oxide for magnetic properties, along with metals and semiconductors to enhance triboelectric and superflow characteristics.

The combination of organic and inorganic materials in toner powders ensures stability and adhesion to paper but renders them nearly non-biodegradable and environmentally harmful. Their persistence in the ecosystem poses significant environmental threats, highlighting the urgent need for sustainable management strategies (Nakadate et al., 2018; Pirela et al., 2017). To establish suitable storage conditions for waste toner powder and enable its transformation into high-value products, it is crucial to categorize cartridge types—such as inkjet, laser, and duplicator cartridges—and understand their core components. Inkjet printers use inks containing harmful chemicals like butyl urea, cyclohexanone, ethylene glycol, and sulfur-based dyes, which release volatile organic solvents during printing and contribute to environmental pollution (Aydemir et al., 2020). Additionally, frequent cartridge replacements, especially in home printers with black, cyan, magenta, and yellow cartridges, exacerbate waste generation. Laser printers and copiers, on the other hand, utilize dry or wet toners. Dry toners are composed of acrylic and styrene powders mixed with color pigments, while liquid toners contain acrylic resins and dyes to produce vibrant images. These toners are primarily made up of plastic resins—typically 45-90% styrene and acrylic polymers—and may also include iron oxide for magnetic properties, as well as metals and semiconductors to enhance functionality (Vucinic et al., 2013). While these materials ensure toner stability and strong adhesion to paper, they are highly resistant to biodegradation, posing significant environmental challenges. The persistence of these materials in ecosystems highlights the critical need for effective waste management and recycling solutions (Nakadate et al., 2018; Pirela et al., 2017).

Considering the toner powder composition summarized above, it has been shown that waste toner powder not only poses environmental and human health risks but also possesses valuable properties, making it a waste material worth (Parthasarathy 2021). evaluating et al.. Consequently, studies various have been conducted in recent years to explore its potential applications (Saini et al., 2020; Bhongade et al., 2019; Saini et al., 2019; Babar et al., 2019; Akilarasan et al., 2018; Kuma et al., 2018). The scope of these studies includes the following: the production of waste toner-derived carbon/Fe<sub>3</sub>O<sub>4</sub> nanocomposites for high-performance supercapacitors (Subramani et al., 2019); the creation of activated carbon as a promising anode for sodium-ion batteries (Uttam et al., 2019; Arjunan et al., 2021); the one-pot conversion of waste toner powder into 3D graphene oxide hydrogel (Tian et al., 2019); the production of micro sorbents from waste toner for use as lowcost magnetic solid-phase extraction adsorbents for Pb analysis (Yu et al., 2022); the development of 3D graphene oxide hydrogels derived from waste toner as adsorbents (Tian et al., 2021); the synthesis of magnetic nanocomposites for the removal of Cr (Zhu et al., 2018); and the creation of low-cost, high-activity, and highly reusable for persulfate-based engineered catalysts advanced oxidation processes in wastewater treatment (Huang et al., 2022). Other applications include the use of waste toner carbon in fully

printable mesoscopic perovskite solar cells (Ma et 2021) and the design of al., cheap. environmentally friendly microwave absorbers from waste toner powders (Habib et al., 2021). However, studies focusing on the evaluation of waste toner powder in the energy sector remain limited. No industrial-scale research has been identified; current studies are confined to laboratory-scale R&D efforts. Examples include hydrogen production from waste toner powder activated by Ni under visible light (Zhang et al., 2022). vacuum pyrolysis and the product dispersion/characterization of toner waste powder (Dong et al., 2017), and the production of a highefficiency 3D solar evaporator derived from waste egg trays and toner for fresh water generation (Ivan et al., 2022).

No studies have been identified on the evaluation of waste toner powder as an energy source in direct combustion processes. However, Patronov and Tonchev (2011) highlighted that toner cartridges and waste toner powder have a high calorific value (approximately 30 MJ/kg), exceeding that of traditional fossil fuels, making them a viable fuel option under controlled combustion conditions. They also cautioned that uncontrolled combustion could result in the release of polycyclic aromatic hydrocarbons (PAH), furans, and dioxins, leading to significant environmental pollution. The increasing environmental concerns associated with fossil fuels, such as greenhouse gas emissions, acid rain, global warming, and climate change, have underscored the growing importance of biofuels as a renewable and clean energy source (Banks et al., 2016). In our country, energy consumption continues to rise alongside improvements in living standards and industrialization, resulting in heavy dependence on fossil fuels. Thus, adopting bioenergy as a renewable resource is crucial to reducing national reliance on foreign energy and enhancing energy security. The furniture factory waste dust planned for use in this study is primarily lignocellulosic biomass, consisting of chopping dust generated during furniture production that can remain suspended in the air. This biomass can be classified as a carbon-neutral fuel and a clean energy source, with significantly lower sulfur and nitrogen content compared to fossil fuels. Combustion of fossil fuels is known to produce minimal  $SO_x$  and  $NO_x$  emissions (Kemper, 2015), making the use of lignocellulosic biomass a cleaner alternative. In industrialized nations, waste disposal, recycling, and the incorporation of waste into a circular economy play vital roles in ensuring the balanced and sustainable use of national resources. Recycling, recovery, and energy production are increasingly viewed as essential strategies for minimizing the volume of waste sent to landfills.

Plastic-containing wastes, such as those comprising 45–90% of waste toner powder, are a significant component of solid waste management

due to their high organic content and environmental impact. These wastes also possess high calorific values compared to traditional biomass and coal. For instance, the calorific values of dry softwood, sub-bituminous coal, and bituminous coal are 19.2, ~20-21, and ~28 MJ/kg, respectively, while polyethylene (PE) and polypropylene (PP) offer calorific values of 41.80 and 30.90 MJ/kg, respectively. Plastic resins are particularly suitable as binders for biomass resources because of their excellent fluidity, tensile strength, and hydrophobicity, enabling the creation of fuel pellets with enhanced physical strength.

However, while direct combustion of high-calorific plastics or plastic-containing wastes can be an effective waste management strategy, it generates significant pollutants, including gases, particulates, and solid residues (ash), that contribute to air pollution. Major acidic gases such as HCl, SO<sub>2</sub>, and even HF or HCN are released during combustion, along with other pollutants like NOx (NO and NO<sub>2</sub>), CO, and volatile organic compounds (Takasuga et al., 2003; Werther, 2007). Particulates, including PM2.5 and PM10, pose direct health risks by entering the respiratory systems of humans and animals (Xing et al., 2016). Additionally, the combustion of plastics produces toxic chemicals such as polychlorinated dibenzo-p-dioxins (PCDD), polycyclic dibenzofurans (PCDF), aromatic hydrocarbons (PAH), pentachlorophenols (PCP), polychlorobenzenes (PCB), hexabromocyclodecanes (HBCD). and polybrominated diphenyl ethers (PBDE), further exacerbating environmental concerns (Verma et al., 2016). Metal pollutants can also arise due to metal-containing additives used in plastic production. Nevertheless, co-burning plastics with biomass have been shown to produce fewer pollutants compared to burning plastics alone (Emadi et al., 2017; Distler and Sitzmann, 2018; Tomsej et al., 2018).

This study aims to address the identified gaps in the current literature by investigating the usability of waste toner powder as an energy resource, particularly in the production of bio-briquettes. It seeks to evaluate its combustion characteristics under controlled conditions, assess its environmental impacts, and explore its potential to contribute to renewable energy solutions. By doing so, the study provides practical insights into integrating waste management with sustainable energy production.

#### 2. EXPERIMENTAL SECTION

#### 2.1. Materials and Sample Preparation

WTP samples (Figure 1) were obtained from a facility (Filling Market Information Technology, Education, Electrical Electronics, E-Commerce, Security Systems, Import-Export, Marketing, Industry, and Trade Limited Company) in the organized industrial zone of Elazig, specifically

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established for recycling toner cartridges. The powder (WTP) waste toner structure was characterized to investigate its potential applications. The samples were stored under suitable conditions to preserve their properties for subsequent analysis. The structural, morphological, and fuel properties of the WTP were analyzed comprehensively, and the obtained results were interpreted to understand its behavior and potential usability.



Figure 1: Supplied waste toner powder sample used in the study.

#### Structural and Morphological Characterization

The structural and morphological properties of WTP were analyzed using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), atomic absorption spectroscopy (AAS), and particle size distribution analyses.

✓ **FTIR Analysis:** To identify the functional groups in the WTP structure, measurements were conducted in the 400-4000 cm<sup>-1</sup> range with 45 scans per sample using a Shimadzu IRSipirit FTIR spectrometer. This method provided insights into the chemical bonds and compounds present in the toner powder.

✓ **SEM-EDX Analysis:** Surface morphology and elemental composition of WTP were determined using a JEOL JSM 7001F scanning electron microscope. High-resolution imaging enabled the visualization of particle shapes, sizes, and surface characteristics, while EDX provided elemental analysis of the material.

✓ AAS Analysis: To quantify the iron content, which is crucial for evaluating the material's magnetic properties, a Perkin-Elmer AAS 3100 Atomic Absorption Spectrophotometer was employed. This ensured precise and accurate measurements of metallic components.

✓ **Particle Size Distribution:** Particle size analysis was conducted in two different dispersive media (toluene and benzene) to assess the dispersion behavior of WTP in sedimentary environments. A PSS Nicomp Zeta Potential/Particle Sizer 380ZLS was used to measure the size distribution, providing critical information on the material's granularity and distribution uniformity.

#### 2.3. Fuel Property Characterization

The fuel properties of WTP were analyzed through proximate and ultimate analysis, as well as higher heating value (HHV) determination, to evaluate its energy potential.

✓ **Proximate Analysis:** This included the assessment of ash content and volatile matter following ASTM standards. Moisture content was determined using a Mettler LJ16 moisture analyzer, providing insights into the material's combustion characteristics.

✓ **Ultimate Analysis:** Elemental analysis for carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) content was performed using a LECO CHNS-932 elemental analyzer. This allowed for the evaluation of the chemical composition and combustion efficiency of the material.

✓ **Higher Heating Value (HHV):** The energy content of WTP was determined to assess its viability as a biofuel. HHV measurements provided a quantitative understanding of its calorific value, essential for energy recovery applications.

#### 2.4. Experimental Design and Conditions

To ensure reliable and repeatable results, all analyses were performed under controlled laboratory conditions using calibrated instruments. Standard methodologies and protocols were adhered to throughout the study, ensuring compliance with international standards. Dispersive media were selected based on their compatibility with toner powder particles to achieve accurate dispersion behavior analysis.

#### 3. RESULTS AND DISCUSSION

#### **3.1. Suitability for Thermal Conversion Processes**

The moisture content of waste toner powder (WTP) (Table 1) was measured at 2.67%, which was significantly below the maximum threshold of 10% required for effective thermal conversion processes such as pyrolysis and combustion. This low moisture level ensured minimal energy loss during the drying phase, making WTP a highly suitable candidate for thermal transformation without the need for energy-intensive pre-drying. This characteristic supported its economic feasibility for energy recovery applications.

## **3.2. Combustion Characteristics and Proximate Analysis**

The high volatile matter (VM) content of 88.38% by weight indicates excellent combustion properties, as volatile components facilitated rapid ignition and flame stability. The low ash content (4.91% by weight) further enhanced the suitability of WTP for combustion processes by minimizing operational issues such as slagging, fouling, and residue management. Low ash fuels were also desirable for reducing post-combustion disposal costs and maximizing energy recovery efficiency. The fixed carbon (FC) content of 4.04% suggested that the primary combustion process relied more on the release of volatile gases rather than prolonged carbon combustion. Additionally, the HHV of 35.56 MJ/kg positioned WTP as an intermediate energy source, suitable for applications requiring medium calorific value fuels, such as biomass co-firing systems.

# **3.3. Ultimate Analysis and Environmental Considerations**

The carbon content (32.12%) was a significant parameter in determining the energy density of the examined material, and it was typical for biomass or low-carbon fuels. The hydrogen content (9.245%) provided insight into volatile components and combustion characteristics, representing a moderateto-high level that significantly contributed to energy potential. The nitrogen content (1.975%) was quite low, which was an environmentally favorable indicator as it implied reduced NOx emissions during combustion.

The oxygen content (53.35%) was relatively high, commonly observed in biomass or oxygen-rich materials, although its contribution to energy value was limited. The sulfur content (3.289%) was a parameter of environmental concern, considered relatively high, potentially leading to SOx emissions during combustion. The proportion of other elements (0.024%) was very low and could be considered negligible in the analysis.

#### 3.4. Iron Content and Ash Composition

To evaluate the inorganic composition of WTP, samples were calcined at 950 °C in a muffle furnace, and the iron content was measured using atomic absorption spectroscopy (AAS). The results indicated an iron content of 0.56%, which was relatively low and comparable to traditional biomass compositions. The low iron content can simplify the fuel preparation workflow bv eliminating the need for additional pretreatment processes, such as iron recovery. Minimal iron content ensures that the ash produced during combustion will not pose significant environmental aligning WTP with sustainable waste risks. management practices. Low metallic content reduces the risk of slag formation during combustion, ensuring smooth operational efficiency.

Ultimate analysis	Value (wt. %)	Proximate analysis	Value (wt. %)
С	32.12	Volatile matter (VM)	88.38
Н	9.245	Ash (A)	4.91
N	1.975	Moisture (M)	2.67
<b>O</b> *	53.35	Fixed carbon* (FC)	4.04
S	3.289	HHV (exp.) MJ/kg	35.56
Other	0.024		

Table 1: Proximate and ultimate analysis result of toner powder (\*: determined by the difference).

# 3.5. Insights from Particle Composition and Behavior

Plastic and inorganic components in WTP may play an important role in combustion behavior, with plastic resins potentially contributing to its calorific value and providing effective binding properties when blended with other biomass sources for fuel pellet production. This is because toner powder is known to contain carbon black, polymethyl methacrylate, styrene acrylate copolymer, and polypropylene, as well as inorganics such as iron and manganese, titanium, oxides. silicon (Yordanova et al. 2014). Although toner powder is highly hydrophobic, the presence of polymeric materials like polymethyl methacrylate, polypropylene, and styrene acrylate copolymer makes it a potential filler or binding agent. the polarity difference between However. hydrophilic waste biomass sources and hydrophobic polymers like polyester may lead to weak interfacial bonding, which can affect the tensile behavior of composites (Daniel et.al 2022).

These results collectively demonstrated that waste toner powder was a promising alternative energy resource. Its low moisture and ash content, combined with high volatile matter and HHV, made it suitable for thermal conversion processes, particularly combustion and pyrolysis. While the nitrogen and sulfur content highlighted a need for emission control measures, the overall composition of WTP aligned well with sustainable energy recovery objectives. The absence of significant iron content further enhanced its practicality by reducing the need for pre-treatment and minimizing environmental risks. Future studies should focus on optimizing combustion parameters and exploring co-firing opportunities with conventional biomass to maximize the efficiency of WTP as a renewable energy source.

#### **3.6. FTIR Analysis of Waste Toner Powder:** Functional Groups and Composition

The FTIR spectrum of waste toner powder (WTP) (Figure 2) revealed key absorption bands that provided critical insights into its chemical composition, supported by a corresponding library analysis. A broad band around 3250 cm<sup>-1</sup> corresponded to O-H stretching vibrations. indicating the presence of hydroxyl groups, likely originating from residual moisture or additives. These polar functional groups contributed minor hydrophilic characteristics to the toner powder. The peaks at 2920-2850 cm<sup>-1</sup> were characteristic of C-H stretching vibrations in aliphatic hydrocarbons, such as CH<sub>2</sub> and CH<sub>3</sub> groups, which suggested the presence of polymer backbones like styrene and acrylate. A sharp peak at 1750 cm<sup>-1</sup> was associated with C=O stretching vibrations, indicative of ester or ketone functional groups, confirming acrylate-based polymers, such as styrene-acrylate copolymers, commonly found in toner formulations.



	Score	Library	Name	Comment
1	853	169 - ATR-Polymer2	D_Styrene_AllylAlcohol	Styrene/Allyl Alcohol Copolymer(Hydroxyl content 5.4-6.0%) DuraSamplIR-II
2	799	1 - ATR-Polymer2	D_ABS	Acrylonitrile-butadiene-styrene(A BS) DuraSamplIR-II
3	797	158 - ATR-Polymer2	D PS2	Polystyrene DuraSamplIR-II
4	782	25 - ATR-Polymer2	D PS	Polystyrene(PS) DuraSamplIR-I
5	776	170 - ATR-Polymer2	D_Styrene_ButylMethacrylate	Styrene/Butyl Methacrylate 50/50 Copolymer
6	771	26 - ATR-Polymer2	D_SBS	Styrene-Butadiene-Styrene(SBS ) DuraSampIIR-II
7	763	167 - ATR-Polymer2	D_SA-2	Styrene/Acryonitrile(SA) Copolymer(Acrylonitrile content 30%) DuraSampIIR-II
8	724	92 - ATR-Polymer2	D_ABS2	Acrylonitrile/Butadiene/Styrene(A BS) Resin(High Butadiene content) DuraSampIIR-II
9	721	53 - IRs Polymer2	PS	Polystyrene ATR/diamond ATRcorrected
10	719	25 - T-Polymer2	PS	Polystyrene(PS) Transmission(Microscope)

Figure 2: FTIR spectrum of toner powder.

In the 1600-1500 cm<sup>-1</sup> range, distinct peaks represented C=C stretching vibrations from aromatic rings, highlighting the aromatic backbone structure characteristic of polystyrene and its derivatives. These features contributed to the rigidity and thermal stability of the material. Further, the bands in the 1450-1400 cm<sup>-1</sup> region corresponded to C-H bending vibrations from CH2 and CH<sub>3</sub> groups, supporting the presence of aliphatic hydrocarbon chains. The 1250-1000 cm<sup>-1</sup> region displayed strong C-O stretching vibrations, typical of ester groups, accompanied by aromatic C-H bending, confirming the existence of acrylate and ester functionalities. Lastly, the absorption bands between 900-700 cm<sup>-1</sup> corresponded to outof-plane C-H bending vibrations, reinforcing the presence of aromatic systems like polystyrene. The experimental results obtained are consistent with the literature (Fernández et. al. 2022; Yordanova et al. 2014).

The library analysis aligned with the FTIR results, confirming the primary components in the toner powder. Styrene/allyl alcohol copolymer was identified by the O-H stretches at  $3250 \text{ cm}^{-1}$  and C=C peaks aromatic around 1600 cm⁻¹. Acrylonitrile-butadiene-styrene (ABS) was characterized by the C-H stretching vibrations near 2900 cm<sup>-1</sup> and weak nitrile group peaks around 2200 cm<sup>-1</sup>. Polystyrene (PS) was supported by aromatic C=C peaks at 1600 cm<sup>-1</sup> and out-of-plane C-H bending at 900-700 cm<sup>-1</sup>. Additionally, methacrylate copolymer was styrene-butyl confirmed by the ester C=O stretching peak at 1750 cm<sup>-1</sup> and aliphatic C-H peaks.

These findings indicated that the toner powder primarily consisted of styrene-based polymers, acrylate-based copolymers, and various additives. Styrene polymers contributed rigidity, thermal stability, and resistance to biodegradation, while acrylate copolymers enhanced flexibility and adhesion properties. Additives like ABS and butyl methacrylate further improved performance characteristics such as heat resistance and print quality.

From an application perspective, the composition highlighted several important implications. The presence of styrene and acrylate polymers confirmed the material's high thermal stability, making it suitable for thermal transformation processes like pyrolysis or combustion. The strong aromatic backbone and low biodegradability emphasized the need for controlled waste management strategies, such as blending with environmental biomass to reduce risks. Additionally, the hydrocarbon-rich composition, coupled with its high calorific value, validated WTP as a promising additive for biofuel production and energy recovery applications.

#### 3.7. Hazardous Substances and Environmental Impacts of Waste Toner Powder

Residual toner powder contains hazardous substances, including plastics, heavy metals, and carcinogenic chemicals such as polycyclic aromatic hydrocarbons (PAHs) and resins, which pose significant environmental and health risks (Bhoi et al., 2014). The primary polymeric component, styrene acrylate copolymer, accounts for the majority of the toner composition and is characterized by its high molecular weight. This property makes it highly resistant to biodegradation, allowing the material to persist in ecosystems for extended periods without significant decomposition. The low water solubility of toner powder further limits its mobility in landfill environments, but it also reduces the likelihood of leaching. However, the heterogeneous morphological and chemical composition of WTP complicates predictions about its degradation behavior under varying landfill conditions (NICNAS, 1991; Yordanova et al., 2012; Yordanova et al., 2019; Kyoseva et al., 2011). Consequently, long-term storage of waste toner powder is considered hazardous due to the potential for unforeseen environmental reactions over time.

The SEM-EDX analysis provided critical insights into the surface morphology and elemental composition of waste toner powder. The SEM micrograph (Figure 3) revealed an irregular granular structure with particle sizes ranging between 4 and 8  $\mu$ m. This morphology, characterized by a high surface area, could have enhanced combustion dynamics when WTP was used as a fuel.

The EDX spectrum and corresponding data highlighted the elemental composition of WTP. The dominant element, carbon (C), constituting 80.50% by weight, confirmed the organic nature of the toner powder. The high carbon content aligned with the material's high volatile matter content (88.38%) observed in the proximate analysis, makes it a suitable candidate for thermal conversion processes. At 13.76% by weight, oxygen was associated with both the polymeric materials and inorganic oxides present in the sample. Oxygen content was critical for combustion processes, influencing the material's ignition and flame stability. The experimental results obtained are consistent with the literature (Fernández et. al. 2022).



**Figure 3:** SEM-EDX analysis of waste toner powder, showing its granular morphology and elemental composition critical for evaluating its potential in biofuel applications.

Silicon (Si) and calcium (Ca) elements, present at 5.07% and 0.67% by weight, respectively, originated from fillers and stabilizers commonly used in toner formulations. While low in concentration, these inorganic components may have influenced ash behavior during combustion, such as melting characteristics and slag formation. Given its plasticrich composition, WTP posed challenges in direct combustion due to the potential release of hazardous emissions such as PAHs and dioxins. However, blending WTP with biomass offered a practical solution to mitigate its environmental drawbacks while leveraging its high energy content. The high carbon and volatile matter content of WTP enhanced its combustion efficiency, while the low ash and moisture content minimized operational challenges and post-combustion residue.

To balance the risks and benefits, it was recommended to limit the proportion of WTP to 8-10% in biofuel mixtures. This dilution strategy ensured that the negative impacts of its plastic composition were mitigated while maintaining desirable fuel characteristics. The low calcium and silicon content observed in the EDX results further supported the material's suitability for blending, as these elements were unlikely to cause significant slagging or fouling during combustion. The hazardous substances and environmental risks associated with waste toner powder underscored the importance of managing its use in a controlled manner. The SEM-EDX analysis revealed a composition that was highly favorable for energy recovery when integrated with biomass, provided that appropriate blending ratios were maintained. Future research should focus on optimizing the blending process, controlling emissions, and evaluating long-term combustion efficiency to fully realize the potential of WTP as a renewable energy resource.

# **3.8. Particle Size Distribution Analysis and Solvent Effectiveness**

The particle size distribution analysis of waste toner powder (Figure 4) in different solvents revealed significant variations in their dispersive effectiveness. In toluene, the particle size distribution was relatively narrow, with a mean diameter of 182.6 nm and a standard deviation of 147.2 nm. The Gaussian distribution was wellcentered, with the majority of particles falling below 400 nm, indicating a uniform dispersion. This suggested that toluene provided favorable interactions with toner components, likely due to better solubility and compatibility with its Taşar, Ş. et al., JOTCSB, 2025, 8(1), 97-110.

polymeric structure. In contrast, benzene showed a broader particle size distribution with a mean diameter of 308.4 nm and a much higher standard deviation of 475.2 nm. This indicated the presence of larger particles and significant agglomeration, demonstrating that benzene was less effective as a dispersing medium. The experimental results obtained are consistent with the literature (Fernández et. al. 2022).

The comparison underscored the superior performance of toluene in achieving a consistent and predictable particle size distribution. Toluene's stronger interactions with toner particles facilitated better dispersion, breaking down agglomerates and ensuring more uniform particle sizes. Benzene, while capable of dispersing the toner powder, exhibited limitations such as broader size variability and particle clustering, which may have hindered its applicability in processes requiring precise particle size control. Overall, the findings suggested that toluene should have been prioritized for applications requiring uniform dispersion, while benzene could have been reserved for less critical uses where variability was less of a concern.

The presence of fine toner particles (<10  $\mu$ m) poses significant health risks, as these particles can remain suspended in the air for extended periods, causing respiratory irritation and long-term damage to living organisms (Salhofer et al., 2011; Nakadate et al., 2018; Pirela et al., 2017). This issue underscores the importance of selecting an appropriate dispersive medium during processing to minimize the generation of respirable particles. Fine particles not only present health hazards but also create challenges in storage and transportation, as they are prone to aggregation, contamination, and dispersion, increasing handling difficulties and safety concerns.



Figure 4: The particle size distribution of waste toner powder (a.Toluene-b.Benzene).

To address these issues, utilizing waste toner powder (WTP) in pellet or briquette form offers a practical solution. By consolidating fine toner particles into larger, denser forms, the risk of airborne particle

dispersion is significantly reduced, enhancing safety during handling, storage, and transportation. This approach also improves logistical efficiency by increasing the bulk density of the material, reducing storage space requirements, and lowering transportation costs.

From an environmental and energy recovery perspective, the pelletization of WTP presents further advantages. Structured forms like pellets or briquettes allow for more controlled and uniform combustion, improving thermal efficiency and reducing the emission of fine particulate matter during energy recovery processes. Additionally, blending WTP with biomass, such as powder, not only mitigates the risks associated with WTP's plastic content but also enhances the biofuel's overall performance. The resulting fuel exhibits high calorific value, better thermal efficiency, and cleaner flue gas emissions, making it an environmentally friendly alternative.

#### 4. CONCLUSION

Our study highlights the potential of waste toner powder (WTP) in the production of bio-briquettes for energy generation. Experiments have shown that WTP possesses a high calorific value (35.56 MJ/kg) and exhibits strong binding properties, making it a promising raw material for biobriquette production. Proximate analysis results indicate that WTP contains 88.38% volatile matter and has low ash (4.91%) and moisture content (2.67%). Additionally, the ultimate analysis reveals a high carbon content (32.12%) and low nitrogen levels (1.98%), indicating its potential for low NOx emissions during combustion. These results demonstrate that WTP is a valuable resource for both environmental sustainability and energy efficiency.

The results have shown that waste toner powder (WTP) is a valuable material to be considered in bio-briquette production. Its high calorific value and strong binding properties highlight its potential as an energy source. Considering the particle size and sulfur/nitrogen contents of WTP, the study concluded that the most effective, suitable, and economical method for utilizing this waste as biofuel is producing biofuel pellets/briquettes by mixing it with powdered biomass waste sources, such as furniture factory waste dust (a lignocellulosic biomass source), in specific proportions.

Finally, utilizing WTP, a material known for causing long-term environmental pollution, as an energy resource would bring significant environmental and economic benefits. Transforming WTP into a highvalue-added product not only addresses landfill sustainability but also contributes to the circular economy by reducing waste and promoting energy recovery. This innovative application has the potential to align with global energy and environmental goals through sustainable waste management practices.

#### **5. CONFLICT OF INTEREST**

There is no need to obtain permission from the ethics committee to prepare the article. There is no conflict of interest with any person/institution in the prepared article.

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#### 7. REFERENCES

- Aydemir, C., & Ozsoy, S. A. (2020). Environmental impact of printing ink and printing process. *Journal of Graphic Engineering and Design*, 11, 11–17.
- Akilarasan, M., Kogularasu, S., Chen, S.-M., Chen, T.-W., & Lou, B.-S. (2018). A novel approach to iron oxide separation from e-waste and bisphenol A detection in thermal paper receipts using recovered nanocomposites. RSC Advances, 8(70), 39870-39878. https://doi.org/10.1039/C8RA08017H
- Arjunan, P., Kouthaman, M., Kannan, K., Diwakar, K., Priyanka, V., Subadevi, R., & Sivakumar, M. (2021). Study on efficient electrode from electronic waste renewed carbon material for sodium battery applications. Journal of Environmental Chemical Engineering, 9(2), 105024. https://doi.org/10.1016/j.jece.2021.105024
- Babar, S., Gavade, N., Shinde, H., Gore, A., Mahajan, P., Lee, K. H., Bhuse, V., & Garadkar, K. (2019). An innovative transformation of waste toner powder into magnetic g-C3N4-Fe2O3 photocatalyst: Sustainable e-waste management. *Journal* of Environmental Chemical Engineering, 7(2), 103041. https://doi.org/10.1016/j.jece.2019.103041
- Banks, S. W., Nowakowski, D. J., & Bridgwater, A. V. (2016). Impact of potassium and phosphorus in biomass on the properties of fast pyrolysis bio-oil. *Energy & Fuels*, 30(10), 8009–8018.
- Bhongade, T., Gogaram, Gautam, D. M., & Vijayakumar, R. P. (2019). Synthesis of MWCNTs using waste toner powder as carbon source by chemical vapor deposition

Taşar, Ş. et al., JOTCSB, 2025, 8(1), 97-110.

method. Fullerenes, Nanotubes and Carbon Nanostructures, 27(11), 864-872. https://doi.org/10.1080/1536383X.2019.165 2169

- Bhoi, V. N., & Shah, T. (2014). E-waste: A new environmental challenge. *IJARCSSE*, *4*, 442-447.
- Cui, J., & Forssberg, E. (2003). Mechanical recycling of waste electric and electronic equipment: A review. *Journal of Hazardous Materials*, 99, 243–263.
- Daniel-Mkpume, C. C., Ahaiwe, R. C., Ifenatuorah, C. L., Ike-Eze, I. C. E., Aigbodion, V. S., Egoigwe, S. V., & Okonkwo, E. G. (2022). Potential end of life application of African star apple shell and waste toner powder as composite filler materials. Journal of Material Cycles and Waste Management, 24(2), 680-691.
- Devin, N., Perkins, B. S., Brune Drisse, M. N., Nxele, T., & Sly, P. (2014). E-waste: A global hazard. *Annals of Global Health*, 80, 286– 295.
- Distler, T., & Sitzmann, W. (2018). An investigation on additives for pelletizing highly torrefied biomass. *Biofuels, Bioproducts and Biorefining*, 12(6), 958–965.
- Dong, L., et al. (2017). Pyrolysis routine of organics and parameter optimization of vacuum gasification for recovering hazardous waste toner. ACS Sustainable Chemistry & Engineering, 5(11), 10038-10045. https://doi.org/10.1021/acssuschemeng.7b0 2024
- Emadi, B., Iroba, K. L., & Tabil, L. G. (2017). Effect of polymer plastic binder on mechanical, storage, and combustion characteristics of torrefied and pelletized herbaceous biomass. *Applied Energy*, 198, 312–319.
- Fernández, B., Ayala, J., Del Valle, E., Martínez-Blanco, D., Castañón, A. M., & Menéndez-Aguado, J. M. (2022). Recycling of waste toner powder as adsorbent to remove aqueous heavy metals. *Materials*, 15(12), 4150.
- Forti, V., Balde, C. P., Kuehr, R., & Bel, G. (2020). *The Global E-Waste Monitor 2020: Quantities, Flows, and the Circular Economy Potential*. United Nations University.
- Gaikwad, V., Ghose, A., Cholake, S., Rawal, A., Iwato, M., & Sahajwalla, V. (2018). Transformation of e-waste plastics into sustainable filaments for 3D printing. ACS

Sustainable Chemistry & Engineering, 6(11), 14432-14440. https://doi.org/10.1021/acssuschemeng.8b0

https://doi.org/10.1021/acssuschemeng.8b0 3105

- Habib, H., Atassi, Y., Salloum, A., Nasser Ali, N., & Jafarian, M. (2021). An eco-friendly, costeffective, lightweight microwave absorber based on waste toner. *Journal of Electronic Materials*, 50(4), 2049–2056. <u>https://doi.org/10.1007/s11664-020-08679-6</u>
- Huang, R., Yang, J., Cao, Y., Dionysiou, D. D., & Wang, C. (2022). Peroxymonosulfate catalytic degradation of persistent organic pollutants by engineered catalyst of selfdoped iron/carbon nanocomposite derived from waste toner powder. *Separation and Purification Technology*, 291, 120963. <u>https://doi.org/10.1016/j.seppur.2022.12096</u> <u>3</u>
- Ivan, N. A. S., et al. (2022). Waste egg tray and toner-derived highly efficient 3D solar evaporator for freshwater generation. ACS Applied Materials & Interfaces, 14(6), 7936-7948. https://doi.org/10.1021/acsami.1c22215
- Kemper, J. (2015). Biomass and carbon dioxide capture and storage: A review. International Journal of Greenhouse Gas Control, 40, 401– 430.
- Kyoseva, V., Todorova, E., & Dombalov, I. (2011). The most common questions on the use of municipal solid waste as raw material and energy resource. ISBN 978-954-92844-1-6.
- Kumar, U., Gaikwad, V., & Sahajwalla, V. (2018). Transformation of waste toner to iron using e-waste plastics as a carbon resource. Journal of Cleaner Production, 192, 244-251. <u>https://doi.org/10.1016/j.jclepro.2018.05.01</u> <u>0</u>
- Li, J., Lu, H., Guo, J., Xu, Z., & Zhou, Y. (2007). Recycle technology for recovering resources and products from waste printed circuit boards. *Environmental Science & Technology*, 41, 1995–2000.
- Ma, D., Sheng, J., Hao, Y., Zhong, Y., & Wu, W. (2021). Photovoltaic green application of waste toner carbon on fully printable mesoscopic perovskite solar cells. *Solar Energy*, 228, 439-446. <u>https://doi.org/10.1016/j.solener.2021.09.05</u> 1
- Nakadate, T., Yamano, Y., Yamauchi, T., Okubo, S., & Nagashima, D. (2018). Assessing the chronic respiratory health risk associated with inhalation exposure to powdered toner

Taşar, Ş. et al., JOTCSB, 2025, 8(1), 97-110.

for printing in actual working conditions: A cohort study on occupationally exposed workers over 10 years. *BMJ Open*, *8*, e022049. https://doi.org/10.1136/bmjopen-2018-022049

- NICNAS. (1991). Full public report: Styreneacrylate copolymer. National Industrial Chemicals Notification and Assessment Scheme.
- Nnorom, I. C., & Osibanjo, O. (2008). Overview of electronic waste (e-waste) management practices and legislations, and their poor applications in the developing countries. *Resources, Conservation and Recycling*, 52, 843–858.
- Park, Y., & Fray, D. (2009). Recovery of high purity precious metals from printed circuit boards. *Journal of Hazardous Materials*, 164, 1152-1158.
- Parthasarathy, M. (2021). Challenges and emerging trends in toner waste recycling: A review. *Recycling*, 6(3), 57. <u>https://doi.org/10.3390/recycling6030057</u>
- Patronov, G., & Tonchev, D. (2011). Waste toners and cartridges—Utilization option. *University* of Plovdiv "Paisii Hilendarski".
- Pirela, S. V., Martin, J., Bello, D., & Demokritou, P. (2017). Nanoparticle exposures from nanoenabled toner-based printing equipment and human health: State of science and future research needs. *Critical Reviews in Toxicology*, 47, 678–704.
- Robinson, B. (2009). E-waste: An assessment of global production and environmental impacts. *Science of the Total Environment*, 408, 183–191.
- Saini, D., Aggarwal, R., Anand, S. R., & Sonkar, S. K. (2019). Sunlight-induced photodegradation of toxic azo dye by selfdoped iron oxide nano-carbon from waste printer ink. *Solar Energy*, *193*, 65-73. <u>https://doi.org/10.1016/j.solener.2019.09.02</u> <u>2</u>
- Saini, D., Aggarwal, R., Anand, S. R., Satrawala, N., & Joshi, R. K. (2020). Sustainable feasibility of waste printer ink to magnetically separable iron oxide-doped nanocarbons for styrene oxidation. *Materials Today Chemistry*, 16, 100256. https://doi.org/10.1016/j.mtchem.2020.1002 56
- Salhofer, S., & Tesar, M. (2011). Assessment of removal of components containing hazardous substances from small WEEE in

Austria. Journal of Hazardous Materials, 186, 1481–1488. https://doi.org/10.1016/j.jhazmat.2010.12.0 46

- Subramani, K., Govindarajan, K., Sundaramoorthy, S., & Marappan, S. (2019). Waste tonerderived carbon/Fe3O4 nanocomposite for high-performance supercapacitor. ACS Omega, 4(14), 15798-15805. https://doi.org/10.1021/acsomega.9b01337
- Takasuga, T., Makino, T., Umetsu, N., & Senthilkumar, K. (2003). Quantitative analysis of toxic compounds formed from combustion of some plastic materials and newspaper. *Organohalogen Compounds*, 63, 86–89.
- Tian, Z., Cao, K., Bai, S., & He, G. (2019). One-pot transformation of waste toner powder into 3D graphene oxide hydrogel. ACS Sustainable Chemistry & Engineering, 7(1), 496-501. https://doi.org/10.1021/acssuschemeng.8b0 3997
- Tian, Z., Sun, L., Tian, H., Cao, K., Bai, S., Li, J., & Zhu, Q. (2021). 3D graphene oxide hydrogel derived from waste toner as adsorbent. *Journal of Nanoscience and Nanotechnology*, 21(10), 5275–5281. <u>https://doi.org/10.1166/jnn.2021.19339</u>
- Tomsej, T., Horak, J., Tomsejova, S., Krpec, K., Klanova, J., Dej, M., & Hopan, F. (2018). The impact of co-combustion of polyethylene plastics and wood in a small residential boiler on emissions of gaseous pollutants. *Chemosphere*, 196, 18-24. https://doi.org/10.1016/j.chemosphere.2017. 12.027
- Uttam, K., Goonetilleke, D., Gaikwad, V., Pramudita, J. C., Joshi, R. K., & Sahajwalla, V. (2019). Activated carbon from e-waste plastics as a promising anode for sodium-ion batteries. *ACS Sustainable Chemistry & Engineering*, 7(12), 10310-10322.
- Veit, H. M., Bernardes, A. M., & others. (2006). Recovery of copper from printed circuit board scraps by mechanical processing and electrometallurgy. Journal of Hazardous Materials, 137(3), 1704–1709. <u>https://doi.org/10.1016/j.jhazmat.2006.05.0</u> 08
- Verma, R., Vinoda, K. S., Papireddy, M., & Gowda, A. N. (2016). Toxic pollutants from plastic waste—a review. *Procedia Environmental Sciences*, 35, 701–708.
Taşar, Ş. et al., JOTCSB, 2025, 8(1), 97-110.

- Vucinic, A. A., Vujevic, D., Mujkic, K., & Novak, M. (2013). Recycling of waste toner in the Republic of Croatia—An environmentally friendly approach. *Chemical Engineering Transactions*, *34*, 121–126.
- Werther, J. (2007). Gaseous emissions from waste combustion. *Journal of Hazardous Materials*, *144*(3), 604-613. https://doi.org/10.1016/j.jhazmat.2007.02.0 17
- Wu, J., Li, J., & Xu, Z. (2008). Electrostatic separation for recovering metals and nonmetals from waste printed circuit board: Problems and improvements. Environmental Science & Technology, 42(14), 5272-5276. https://doi.org/10.1021/es800324f
- Xing, Y. F., Xu, Y. H., Shi, M. H., & Lian, Y. X. (2016). The impact of PM2.5 on the human respiratory system. *Journal of Thoracic Disease*, 8(1), E69. https://doi.org/10.21037/jtd.2016.01.14
- Yordanova, D., & Dombalov, I. (2012). Hazardous household waste—Definition and choice of appropriate treatment method. *Proceedings* of the International Conference: Ecology – Interdisciplinary Science and Practice, ISBN 978-954-749-096-3, 365-367.

- Yordanova, D., Angelova, S., & Dombalov, I. (2014). Utilisation options for waste toner powder. *J. Environ. Sci*, *3*, 140-144.
- Yordanova, D., Angelova, S., & Dombalov, I. (2019). Utilisation options for waste toner powder. International Scientific Journal Environmental Science, 8, 140–144.
- Yu, X., Zhu, C., Wang, H., & Wu, Y. (2022). Waste toner-derived micro-materials as low-cost magnetic solid-phase extraction adsorbent for the analysis of trace Pb in environmental and biological samples. Analytical and Bioanalytical Chemistry, 414(7), 2409–2418. https://doi.org/10.1007/s00216-022-03879-x
- Zhang, W., Guan, H., Hu, Y., Wang, W., Hao, L., Yang, X., & Tian, W. (2022). Visible-lightdriven hydrogen evolution from waste toner powder activated by Ni species. Green Chemistry, 24(3), 1335-1341. https://doi.org/10.1039/D1GC03506A
- Zhu, H., Zhou, Y., Wang, S., Wu, X., Hou, J., Yin, W., Feng, K., Wang, X., & Yang, J. (2018). Preparation and application synthesis of magnetic nanocomposite using waste toner for the removal of Cr(VI). RSC Advances, 8(49), 27654-27660.

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**RESEARCH ARTICLE** 



# Optimization of a Reactive Distillation Column by Design Expert Method and Statistical Analysis of the Process

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**Abstract**: The reactive distillation system integrates both reaction and distillation processes in a single operation. When compared to conventional distillation methods, it has been identified as a more efficient system in terms of product yield and cost-effectiveness. This study investigates the effects of operational parameters, specifically feed rate, reflux ratio, and feed temperature, on the methyl acetate yield in a simulated reactive distillation column. Using a design expert approach, the interactions between these parameters and their effects on product yield were demonstrated through 3D graphical representations. Subsequently, optimization studies were conducted using experimental design techniques, resulting in optimized feed rate, reflux ratio, and feed temperature to maximize methyl acetate production. Relationships among variables deemed significant in the simulations were analyzed using three-dimensional graphs, allowing for insights into the process. Additionally, the results showed alignment between the product (methyl acetate) flow rate predictions from simulation and experimental design. The impact of input parameters on the resulting quadratic model was mathematically assessed, and statistical variance analysis (ANOVA) was calculated. As an innovative method in reactive distillation, statistically validated the model's suitability and achieved effective results in terms of yield optimization.

Keywords: Reactive distillation, design expert, optimization, statistical analysis

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# **1. INTRODUCTION**

In the context of industrial processes, designs that maximize efficiency in time, energy, and other resources while maintaining environmental responsibility and minimizing production costs are highly valued. Companies that seek to maintain international competitiveness must achieve their objectives through controlled, efficient production process designs. Today, the importance of sensitivity environmental has increased significantly. Achieving these goals—sustainability, reduced resource use, and green productiondemands that industrial process designs be both efficient. functional and aligning with а responsibility to future generations. This perspective has driven the development of process designs and optimization studies aimed at achieving maximum efficiency with minimal resource use during production.

Reactive distillation combines both chemical reaction and multi-component separation into a single unit. For certain processes, it presents a compelling alternative to conventional systems that employ separate reaction and distillation stages. Although reactive distillation has only been applied in a limited number of industrial cases for years, research and applications in the field have surged in the last decade (Giwa & Karacan, 2012). The benefits of reactive distillation arise when reactions occur at temperatures and pressures that are suitable for distillation. Its primary advantages include eliminating equipment, enabling continuous removal of products from the reaction zone, increasing overall conversion in equilibrium reactions, and reducing both investment and

operational costs. Moreover, it minimizes environmental impact, enhances conversion, improves selectivity, lowers energy consumption, supports challenging separations, and prevents azeotropes (Giwa & Karacan, 2012).

The optimal synthesis of distillation processes remains a critical challenge in chemical process design due to the high investment and operating involved. Recently, mathematical costs programming approaches have gained traction, addressing increasingly complex models. However, the high nonlinearity and difficulties in solving these optimization models have limited the adoption of rigorous methods in industrial applications. Traditionally, direct settings have been used in process industries, where control variables corresponding to a specified steady-state are set for startup, and the system is allowed to stabilize over time. Alternative strategies, including total reflux and zero reflux, have been proposed, often requiring high reboiler heat duty. Because a distillation column's performance is influenced by numerous factors—such as column structure, tray type, component properties, and product specifications-these empirical approaches are effective only in specific cases. Consequently, systematic approaches are required to address these factors comprehensively for distillation column optimization, necessitating methodologies in modeling and optimization (Karacan, 2007).

Reactive distillation (RD) is an important example of process intensification. It is a combination of chemical reaction and multi-component distillation in a counter-current column. The most important advantage in using RD for equilibrium-controlled reactions is the elimination of conversion limitations by continuous removal of products from the reaction zone. The use of RD process can offer several advantages such as reduced downstream processing, utilization of heat of reaction for evaporation of liquid phase, simple temperature control of reactor, possibility of influencing chemical equilibria by removal of products and limitations imposed by azeotropic mixture. All these factors contribute to the growing commercial importance of reactive distillation column (RDC). Reactive distillation is normally applied to some specific processes and one of them is the production of esters. Esters are of great importance to chemical process industries. Among them, acetate esters are important organic solvents widely used in the production of varnishes, ink, synthetic resins, and adhesive agents. They are produced from the reactions of acid and alcohols under an acidic condition. A kev issue in the production of these esters is the low conversion from the reactions. As a result, heavy capital investments and high energy costs are inevitable. The reactive distillation is a very attractive way to reduce these investments and energy costs (Karacan et al., 2019).

Using design expert, RSM technique based on CCD optimization method was used to design the experiments and reboiler temperature, reflux ratio, total feed flow rate, methanol to acetic acid mole ratio, feed locations of acetic acid and methanol and their effects on the conversion of acetic acid as well as on compositions of distillate and bottom products were evaluated. The aim of optimization studies which was performed with RSM is to increase the amount of the product in the RD column by increasing the product flow rates and product purity. The steps to be followed during RSM on the designed process are listed as follows:

• Determine the lower and upper limits for parameters according to the production conditions for the process,

• Operate the process with the developed situation by applying the operating parameters to calculate the value of the response in all simulation trials,

• Obtain a mathematical model showing the dependence of the obtained response on the operating parameters according to the simulation outcomes and test the fit of this model to the simulation outcomes,

• Solve the mathematical model to determine the optimum operating conditions of RD column. Accordingly, the response is considered to be a function of the independent variables (operating parameters). (Aldemir & Ersingün, 2024).

The esterification of methanol and acetic acid to produce methyl acetate in a packed catalytic reactive distillation column was investigated using Indion 180 ion-exchange resin as a catalyst. A regression model was developed based on CCD and experimental data. Using statistical methods, a close fit between the model and experimental data was observed. The model identified optimal conditions for maximizing methyl acetate purity, including a reflux ratio of 1.95, reboiler temperature of 80 °C, and methanol/acetic acid mole ratio of 1.05 (Mallaiah & Reddy, 2016).

novel methodology for the simultaneous optimization of design and operation of a complex reactive distillation process, considering a number of process alternatives (e.g.pre-/side-reactor, sidestripper, additional columns, etc.), was presented. The methodology is illustrated using different case of industrial interest with varying studies separation and reaction characteristics. For easy separations, in terms of relative volatilities and boiling points order, a single reactive distillation column is found to be optimal for both fast and slower kinetics. For operation, chemical reaction equilibrium is the dominant factor. It is demonstrated, however, that the combined effects of separation and reaction must be considered carefully when designing a reactive distillation process (Tsatse et al., 2021).

Optimization of operating parameters for the production of furfuryl alcohol in a reactive distillation column was carried out using response surface methodology (RSM). The key process variables, such as pressure (0.2-1 bar), reflux ratio (1-8), feed ratio (1-2), and residence time (5-20 s), were analyzed to evaluate their influence on the furfuryl alcohol yield. A Box-Behnken experimental design was employed, and the results of the ANOVA study revealed that the feed ratio and reflux ratio had the most significant impact on the process performance. The optimization process identified the optimal operating conditions to be a pressure of 0.4 bar, reflux ratio of 5.6, feed ratio of 1, and residence time of 14 min. Under these optimized conditions, the furfuryl alcohol yield was maximized at 99 %. The effectiveness of the response surface methodology approach in determining the optimal operating parameters for the efficient production of furfuryl alcohol in a reactive distillation column. The findings of this work can be leveraged to guide the design and operation of industrial-scale furfuryl alcohol production facilities, contributing to the efficient and sustainable utilization of this important platform chemical. Further research could explore the scale-up of the process and investigate the economic feasibility of the optimized production system (Amooey, 2024).

Reactive distillation (RD) can be effectively used to improve the selectivity of the intermediate product for complex multi-reaction schemes, which involves using distillation to manipulate the column profiles in the RD column (RDC) to attribute the desired reaction and the manipulating reactions to facilitate separation. As the demand for ethyl methyl carbonate (EMC) has increased significantly due to its structural characteristics, the selective synthesis of EMC from the consecutive transesterification of dimethyl carbonate (DMC) and ethanol (EtOH) in the presence of azeotropes between reactants and products was studied as featured reaction schemes. The basic resin catalyst KC161 is utilized to build the kinetic reaction model and supplement the primary data for the process design. The pilot-scale RD experiments are explored to verify the feasibility and the reliability of the model. The impact of critical operation and structure parameters on the conversion and selectivity of the reaction and the azeotropes formed in the system were analyzed. A hybrid distillation process containing an RDC, pressureswing distillation columns, and a regular distillation column, was designed and optimized based on minimized total annual cost (TAC) using a sequential iterative algorithm. 0. 9997 (mole purity) EMC and 0. 9999 (mole purity) diethyl carbonate (DEC) were obtained with EMC selectivity up to 0.863% (Guo et al., 2024).

This study focuses on simulating methyl acetate production via the esterification reaction in a reactive distillation column. Statistical analysis of the model obtained from the design expert software and the optimization of operating variables were performed. By defining optimal operating conditions for the key variables-feed rate, reflux ratio, and feed temperature—this study aims to design a reactive distillation process that maximizes methyl acetate production with minimal resource use. By refining process designs for optimal product yield through mathematical modeling, statistical analysis, and optimization, this study contributes to creating a competitive, functional, and highly efficient process design. Additionally, this production process, developed with environmental sensitivity in mind, aligns with businesses' primary objective of enhancing profitability.

### 2. EXPERIMENTAL SECTION

#### **2.1. Process Design for Methyl Acetate Production Using Chemcad**

Methyl acetate is produced as a result of the esterification reaction between acetic acid and methanol. In this theoretical study, the process simulation software Chemcad, developed by Chemstations, was used to simulate various experimental conditions within а reactive distillation column, where both separation and reaction occur simultaneously. The primary objective of the design is to establish the most economical conditions for methyl acetate production by evaluating the resources required for investment and operating costs. This entails achieving the highest efficiency in terms of product yield per unit of resource. The system model for the simulation experiments includes feed lines for methanol and acetic acid as inputs to the reactive distillation column, along with a reboiler, condenser, reflux unit, and collection lines for top and bottom products. Through the Chemcaddesigned reactive distillation column system, the operational process was executed, resulting in methyl acetate as the top product and water as the bottom product after separation from other components.

# 2.2. Analysis of Variance and Optimization Using Design Expert Method

Based on the model predictions obtained from the Chemcad simulation outputs, experimental studies were conducted using the trial version of the design expert software. These experiments examined the effects of variables such as feed ratio, reflux ratio, and feed temperature on the yield of methyl acetate. Optimization studies identified the optimal conditions to achieve higher production yield. To support future studies, pairwise interactions between variables were analyzed using generated 3D graphical representations.

Experimental design is a process analysis technique that involves controlling variable changes to determine their effects on the target response. This method allows for the evaluation of the impact of various independent factors on a dependent factor. Statistical methods in experimental design offer significant advantages for optimizing operating conditions, increasing yield, and reducing the number and cost of experiments (Akkuş & Karabudak, 2020).

In comparison to traditional methods, experimental design achieves goals in a shorter time with fewer experiments and lower costs. Its primary advantage lies in examining both the individual and interactive effects of variables, as opposed to traditional methods where only single-variable effects are considered. This comprehensive approach provides more reliable results during the optimization phase (Keyf, 2017).

#### 2.2.1. Response surface methodology

The Response Surface Methodology (RSM) is a set of mathematical and statistical techniques used for modeling and analyzing processes affected by several independent variables, with the goal of optimizing the output. In this study, RSM was applied to optimize the operating parameters for methyl acetate production in the reactive distillation column. The Central Composite Design (CCD), which includes a predefined number of independent variables, was used to assess the effects of these variables on methyl acetate composition. The independent variables were coded at three levels: -1, 0, and +1, where -1 represents the minimum value, +1 the maximum, and 0 the midpoint between these values. The statistical significance of equations was verified (Mallaiah & Reddy, 2016).

RSM has become increasingly popular in scientific research due to its optimization capabilities, ability to create mathematical models of variable interactions, and capacity to identify and establish connections between influential variables (Günay & Bayram, 2021). Table 1 presents the coded values for independent variables in the experimental design for methyl acetate production via reactive distillation.

Table 1. Values Coded for Experimental Design.

Value code	Independent variable	Minimum value (encoded value)	Central value (encoded value)	Maximum value (encoded value)
А	Feed rate	2.5	3.75	5
В	Reflux ratio	1	1.25	1.5
С	Feed temperature(°C)	30	45	60

For instance, the feed temperature ranges from 30 °C to 60 °C, where "-1" corresponds to 30°C, "0" to 45°C, and "+1" to 60°C. The minimum and maximum variable values were determined based on the feasibility of results from the Chemcad simulations.

RSM not only identifies optimal operating conditions but also provides essential data for process design. By integrating first- and secondorder Taylor equations, RSM is a scientific approach used to determine optimal conditions. In RSM, the response (yield) defines the surface of the Taylor expansion curve, with the number of variables playing a critical role in design complexity. As the number of variables increases, the required number of experiments also proportionally rises. Another advantage of RSM is the ability to graphically display the relationship between variables and responses. Equation (1) presents the mathematical model equation developed through experimental design.

Methyl Acetate Mass Flow Rate = 150.44-0.63\*A-13.35\*B+19.32\*C+5.20\*A\*B\*-4.82\*A\*C-0.4 3\*B\*C-32.22\*A<sup>2</sup>-7.13\*C<sup>2</sup>......(1)

# 2.2.2. Analysis of variance (ANOVA) with statistical techniques

In experimental design software, the conditions of interest are termed as "factors." Factors can have two or more levels, which may be determined by the experimenter or may be beyond their control. By applying variance analysis to the observational data obtained from the experiments, this technique identifies whether the factors in question are statistically significant. Analysis of Variance (ANOVA), created by Ronald Aylmer Fisher, is a widely-used technique. In experiments, the characteristic of interest is termed the "response" or dependent variable, which can be quantitative or gualitative. Independent variables, also known as factors, are experimental variables that can be controlled and impact the values the dependent variable will assume (Aldemir, Ersingün & Bayram, 2022).

# **3. RESULTS AND DISCUSSION**

Theoretical studies were conducted using both Chemcad and experimental design software within the reactive distillation process framework. Steadystate experiments in Chemcad determined the operating ranges for feed ratio (2.5-5), reflux ratio (1-1.5), and feed temperature (30-60 °C). Based on these conditions, 20 different experimental sets were generated using the experimental design software. These sets were simulated in Chemcad to obtain methyl acetate yields (kg/h). The data from these simulations were then analyzed within the experimental design framework, and the interactions between variables were visualized in 3D graphical representations to calculate optimal values.

### **3.1. Response Surface Methodology (RSM)** Studies

For independent variables such as feed temperature, feed rate, and reflux ratio (k=3), applying a Central Composite Design (CCD) resulted in 2k=6 central experimental points, out of a total of 20 experiments. These points were selected as the center, while 14 additional points were defined outside the center. Table 2 provides the ranges for the design variables: feed rate, reflux ratio, and feed temperature.

**Table 2:** Variables and their ranges determined for the experimental design method.

Independent variable	Design variable	-1.68(α)	-1	0	+1	+1.68(α)
Feed rate	А	1.64	2.5	3.75	5	5.85
Reflux ratio	В	0.82	1	1.25	1.5	1.67
Feed temperature(°C)	С	19.77	30	45	60	70.22

### **3.2.** Analysis of Variance (ANOVA) Results

Table 3 presents the variance analysis (ANOVA) results for the quadratic model proposed for methyl acetate production. As shown in the ANOVA table, the model's F-value of 4.93 indicates that

the model is both suitable and significant for methyl acetate production. In this study, the correlation coefficient  $R^2$ =0.816, indicating a strong fit between the model and simulation results.

Table 3: Analysis of variance (ANOVA) table of the proposed quadratic model.

Parameters	Mean	Variance	Least mean	F-value	P-value	
	squares		square			
Model	23969.81	9	2663.31	4.93	0.0101	Significant
А	5.36	1	5.36	0.0099	0.9227	
В	2434.06	1	2434.06	4.50	0.0598	
С	5098.61	1	5098.61	9.43	0.0118	
AB	216.11	1	216.11	0.3997	0.5414	
AC	186.05	1	186.05	0.3441	0.5705	
BC	1.48	1	1.48	0.0027	0.9593	
A <sup>2</sup>	14893.87	1	14893.87	27.55	0.0004	
B <sup>2</sup>	1887.31	1	1887.31	3.49	0.0913	
C <sup>2</sup>	718.61	1	718.62	1.33	0.2758	
Residue	5406.73	10	540.67			
Lack	5406.73	5	1081.35			
Error	0	5	0			
Total	29376.54	19				

# **3.3. Effect of Operating Variables on Methyl Acetate Yield**

Table 4 displays the experimental design's suggested operating conditions and product yield values for the reactive distillation process. The

actual values are the methyl acetate mass flow rates obtained from the Chemcad simulations, while the predicted values are those suggested by the response surface methodology within the defined parameter ranges.

Table 4: Methyl acetate mass flow rate values predicted by the model and obtained from the simulation.

Simulation	Feed rate (A)	Reflux ratio (B)	Feed temperature (C) (°C)	Simulation values	Values predicted by the model
1	5	1.5	60	84.29	92.18
2	2.5	1	30	149.21	150.24
3	2.5	1.5	30	168.31	140.32
4	2.5	1	60	67.17	57.95
5	3.75	1.25	19.77	128.07	143.33
6	3.75	1.25	45	149.21	150.24
7	2.5	1.5	60	199.79	162.76

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8	5	1	30	149.21	150.24
9	3.75	0.83	45	89.38	104.87
10	3.75	1.25	45	86.52	58.26
11	3.75	1.25	45	66.61	76.73
12	3.75	1.67	45	87.43	122.04
13	3.75	1.25	45	103.33	95.42
14	3.75	1.25	45	87.88	105.38
15	5	1.5	30	149.21	150.24
16	1.64	1.25	45	149.21	150.24
17	5	1	60	149.21	150.24
18	3.75	1.25	70.22	96.64	97.77
19	3.75	1.25	45	84.29	94.18
20	3.75	1.25	45	68	60.36

# 3.4. 3D Graphics

Figures 1, 2, and 3 provide the 3D graphs generated through experimental design. These graphs illustrate the pairwise interactions between

the input variables—feed rate, reflux ratio, and feed temperature—and their effects on product yield.



Figure 1: Interaction plot of feed rate and reflux rate.



Figure 2: Interaction graph of feed temperature and feed rate.



Figure 3: Interaction plot of feed temperature and reflux rate.

# 3.5. Results of Optimization

To achieve the desired production yield, the appropriate input variables must be optimized. Numerical optimization techniques were employed in the optimization studies conducted via experimental design. The results and graphs from these studies are presented below, and the solution values suggested by the system are listed in Table 5.

**Table 5:** Solutions offered by the system as a result of optimization studies.

Solutions	Feed rate (A)	Reflux r (B)	ratio	Feed temperature (C, °C)	Methyl acetate mass flow rate (kg/h)	Desirability
1	3.58	1.09		60	167.334	0.756
2	3.58	1.09		60	167.333	0.756
3	3.58	1.09		60	167.328	0.756
4	3.56	1.10		60	167.325	0.756

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5	3.60	1.11	59	166.976	0.754	
6	3.56	1.09	60	167.321	0.756	
7	3.70	1.13	60	166.932	0.753	
8	3.56	1.08	60	167.302	0.756	
9	3.60	1.12	60	167.191	0.755	

# **3.6. 3D Graphics Optimized by Experimental Design Method**

Figures 4, 5, and 6 present the 3D optimization graphs obtained through experimental design. These graphs reveal the optimization analysis of product yield based on the pairwise interactions between input variables—feed rate, reflux ratio, and feed temperature. The optimized values suggested by the system, as given in Table 5.7, are as follows: feed rate = 3.58, reflux ratio = 1.09, and feed temperature = 60 °C. The design model predicts an optimal mass flow rate of 167.334 kg/h for these input values.



Figure 4: Interaction graph of reflux rate and feed rate as a result of optimization.



Figure 5: Interaction graph of feed temperature and feed rate as a result of optimization.

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Figure 6: Interaction graph of reflux ratio and feed temperature as a result of optimization.

#### 3.7. Model and Simulation Comparison

Figure 7 illustrates the relationship between the data obtained from 20 experiments conducted according to the algorithm recommended by the experimental design software and the values predicted by the model under identical conditions. The graph compares the predicted methyl acetate

yield with the simulated yield to analyze the agreement between the model and simulation. Since the optimal conditions are defined in terms of feed rate, reflux ratio, and feed temperature, the model and experimental data are observed to be in alignment.



Figure 7: Model and simulation comparison of methyl acetate yield.

The optimization results obtained through experimental design indicate that the optimized input values are feed rate = 3.58, reflux ratio = 1.09, and feed temperature = 60 °C. ANOVA analysis yielded an F-value of 4.93 and  $R^2$ =0.816, with the remaining unexplained 0.184 attributed to uncontrolled external factors not included in the

model. The p-value, calculated at a 95% confidence interval (p < 0.05), confirms the model's validity and applicability.

### 4. CONCLUSION

The reactive distillation system integrates the reaction and distillation processes into a single Compared to conventional distillation unit. methods, it has been identified as a more effective system in terms of product yield and cost efficiency. In this study, the effects of key operational parameters-feed rate, reflux ratio, and feed temperature-on methyl acetate yield were observed in a simulated reactive distillation column. Through a design of experiments approach, the interactions between these parameters and their influence on product yield were illustrated in 3D graphical representations. Optimization studies were then performed using the experimental design approach, where feed rate, reflux ratio, and feed temperature were optimized to achieve maximum methyl acetate production.

Furthermore, a high degree of consistency was observed between the predicted methyl acetate flow rate values from simulation and those derived from experimental design. The effects of input parameters on the resulting quadratic model were mathematically evaluated, and statistical variance analysis (ANOVA) yielded an R<sup>2</sup> value of 0.81. The ANOVA analysis indicated an F-value of 4.93, with the variation corresponding to 1.01%, suggesting that this variability likely resulted from system's disturbance. With an F-value indicating model significance and a p-value of 0.0101 (p < 0.05), the model was deemed statistically significant. The design expert approach, applied as an innovative method in the reactive distillation process, effectively validated the model's suitability and achieved efficient results in terms of yield optimization.

In this study, the optimized values proposed by the system were feed rate = 3.58, reflux ratio = 1.09, and feed temperature = 60 °C. The design model predicted an optimal mass flow rate of 167.334 kg/h for these input variables. Comparing these results with literature findings, it has been reported that a continuous two-feed reactive distillation process benefits from having a shorter distance between the two feed entries and positioning the heavier reactant feed above the lighter one. In terms of cost reduction and energy savings in reactive distillation, rapid optimization results can be achieved by reducing energy requirements (i.e., lower reflux ratio) under optimal feed conditions (Muthia et al., 2019).

# **5. CONFLICT OF INTEREST**

There is no conflict of interest among the authors.

#### 6. REFERENCES

- Akkuş, M.S. & Karabudak, S. (2020). Biyoproses Çalışmalarında Deneysel Tasarım Yönteminin Uygulanması, İleri Mühendislik Çalışmaları ve Teknolojileri Dergisi, 1 (2), 188-197.
- Aldemir, A., Ersingün, D., & Bayram, İ. (2022). Dynamic Simulation of a Reactive Distillation Column for Ethyl Acetate Production: Optimization of Operating Conditions Using Response Surface Methodology. Yüzüncü Yıl Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 27(2), 365-379. https://doi.org/10.53433/yyufbed.1100522
- Amooney, A. A. (2024). Optimization of operating parameters for furfuryl alcohol production in a reactive distillation column using response surface methodology, *Results in Chemistry*, 12-101873. https://doi.org/10.1016/j.rechem.2024.10187 3
- Bayram, İ. & Günay, A. (2021). Tepkimeli damıtma kolonunun dinamik simülasyonu ile deneysel tasarım yöntemi kullanılarak işletim koşullarının optimizasyonu, Yüksek Lisans, Fen Bilimleri Enstitüsü, Kırşehir Ahi Evran Üniversitesi.
- Chemcad v6.5.7. Chemstation Inc.. 3100 Wilcrest Drive Suite 300 Houston TX 77042.
- Design-Expert®, (7.0.0) Trial, Stat-Ease, Inc., Minneapolis, MN, ABD, www.statease.com
- Ersingün, D., & Aldemir, A. (2024). Design and two step process optimization of a reactive distillation column for improving production amount of ethyl acetate and water. Desalination and Water Treatment, 317, 1-12.

https://doi.org/10.1016/j.dwt.2024.100117

- Giwa, A., & Karacan, S. (2012). Decoupling PID Control of a Reactive Packed Distillation Column. International Journal of Engineering Research & Technology (IJERT), 1(6), 1924-1933. url={https://api.semanticscholar.org/Corpusl D:55651871}
- Giwa, A., & Karacan, S. (2012). Simulation and Optimization of Ethyl Acetate Reactive Packed Distillation Process Using Aspen. *TOJSAT:The Online Journal of Science and Technology*, 2(2), 57-63. url={https://api.semanticscholar.org/Corpusl D:55651871}
- Guo, Y., Wang, R., Shu, C., Li, H. &Gao, X. (2024). Selective synthesis of methyl ethyl

carbonate intensified by reactive distillation from consecutive transesterification of methyl carbonate and ethanol. *Separation and Purification Technology*, 338, 126516. https://doi.org/10.1016/j.seppur.2024.12651 6

- Karacan, S., Bayram, İ., & Giwa, A., (2019). Chapter 12: Nonlinear Generalized Predictive Control based on Narimax Model of a ReactivePacked Distillation Column. *Theotetical Inverstigations and Applied Studies in Engineering* (pp.215-230), Bursa: Ekin Publisihing.
- Karacan, F., Özden, Ü., &Karacan, S. (2007).
  Optimization of manufacturing conditions for activated carbon from Turkish lignite by chemical activation using response surface methodology, Applied Thermal Engineering, 27 (7), 1212-1218.
  10.1016/j.applthermaleng.2006.02.046
- Keyf, S. (2017). Deneysel tasarım metodu kullanılarak yüksek performanslı sıvı kromatografisi ile amoksisilin tayini , ÖHÜ Müh. Bilim. Derg., 6 (2), 394-405. https://doi.org/10.28948/ngumuh.341190

- Malliah, M., M., & Reddy, G., V. (2016). Optimization studies on a continuous catalytic reactive distillation column for methyl acetate production with response surface methodology. *Journal of the Taiwan Institute of Chemical Engineers*, 69, 25-40. https://doi.org/10.1016/j.jtice.2016.10.007
- Muthia, R., Ham, A., Jobson, M., Kiss, A. A., (2019). Effect of boiling point rankings and feed locations on the applicability of reactive distillation to quaternary systems, *Chemical Engineering Research and Design*, 145, 184-193. https://doi.org/10.1016/j.cherd.2019.03.014
- Pambudi, L.K. & Wibowo, A.A., 2020, Studi Kasus Pengaruh Tekanan Feed Pada Prepressure Swing Distillation Metil Asetat Berbasis Chemcad, *Distilat Jurnal Teknologi Separasi*, 6 (2), 103-110.
- Tsatse, A., Oudenhoven, S.R.G., Kate, A.J.B., & Sorensen, E. (2021). Optimal design and operation of reactive distillation systems based on a superstructure methodology, *Chemical Engineering Research and Design*, 170, 107-233. https://doi.org/10.1016/j.cherd.2021.03.017

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# Preparation and Characterization of Varying Carbon Black Particle Sizes on Poly(Epichlorohydrin) Elastomer: I. Improving of Curing Kinetics and Mechanical Properties

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Abstract: This study investigates the effect of carbon black (CB) particle size on the curing kinetics and mechanical properties of poly(epichlorohydrin) (H55) elastomers. The curing behavior was analyzed at 170 °C, 180 °C, 190 °C, and 200 °C, using first-order and nth-order kinetic models to determine the activation energy (Ea) and cure rate constant (k). Results indicate that CB significantly accelerates the vulcanization process, reducing the scorch time (ts2) and optimum cure time (t90) while increasing delta torque ( $\Delta$ T) values, which correlates with improved cross-link density. The H55-N330 formulation exhibited the fastest cure rate and the highest delta torque, highlighting its superior curing efficiency. Mechanical testing revealed that adding CB enhanced stiffness, tensile strength, and modulus of elasticity, with the H55-N330 blend showing the highest elastic modulus ( $9.90 \pm 1.07$  MPa), approximately 13 times higher than CB-free H55 (0.70  $\pm$  0.14 MPa). Swelling studies confirmed that CB increases cross-link density, leading to a 54% reduction in swelling ratio for the H55-N330 blend. Additionally, Shore A hardness values doubled with CB incorporation, while compression set values increased. Despite no significant differences in elongation at break, the addition of CB improved overall toughness and durability. These findings suggest that carbon black, particularly N330, significantly improves the curing kinetics, mechanical properties, and cross-link density of H55 elastomers, making them ideal for high-performance rubber applications in automotive, aerospace, and industrial sealing systems.

Keywords: Poly(epichlorohydrin), Carbon Black, Cure Kinetics, Mechanical Properties.

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#### **1. INTRODUCTION**

For about 150 years, developments in rubber technology have produced many useful products with rubber. Due to their elasticity, viscoelastic, mechanical, and chemical properties, rubbers are versatile, meaningful, and unique technological materials for widespread applications in the tire and, automotive, and aviation industries or general rubber products such as gloves, hoses, o-rings, etc. Two leading groups of rubber commonly used in industry are natural rubber and synthetic rubber. Rubber materials consist of many components, such as activators, process oils, curing systems, and fillers. Fillers are a primary component in the rubber industry. They are added on purpose. They lower the material's cost and enhance the compounds' mechanical and dynamic qualities. Fillers add strength and rigidity to elastomers, increase rubber resistance to tearing, abrasion, and bending fatigue, and improve traction and endurance (Zhang et al., 2001). Silica and carbon black (CB) are the most widely used fillers in the rubber industry.

Decades ago, other fillers, such as silica and clay, were frequently utilized in situations where a high

level of reinforcement was not needed. There was a lesser polymer-filler interaction (Mark et al., 1994; Mowdood et al. 2000). Due to the silanol groups on its surface, silica has a high degree of polarity and a hydrophilic surface. Because of this, silica filler cannot be used with non-polar rubbers, including butadiene, styrene-butadiene, and natural rubber (NR), among others. It is well acknowledged that the molecular interactions between the filler and rubber particles cause the reinforcing effects. For the successful use of silica for rubber reinforcement, it has been widely used by modifying the silica surfaces with silane coupling agents to increase the silica-rubber interaction (Noordermeer et al., 2014: Hanifi et al., 2005: Manna et al. 1998).

Another standard filler is carbon black (CB). However, carbon black manufacturing generally leaves a significant carbon footprint. Carbon black is rubber industry's most widely used reinforced filler since World War I. More than 92 percent of CB production worldwide is used for rubber production, particularly in manufacturing tires; these components include inner liners, sidewall carcasses, air sources, belts, conveyor wheels, and specific vibration isolation devices. Around 8.1 million tonnes of carbon black are produced worldwide, ranking among the 50 most advanced industrial chemicals (Fan et al., 2020). Carbon black will be a filler that will continue to be used in rubber product production in the future. The literature on CB fortification of rubber has been reviewed over the last 100 years, and over 10,000 publications have been produced. Although this article includes the words "carbon black," "reinforcement," and "rubber" in its titles, the mechanical reinforcement effect of CB in rubber has been studied in papers generally (Robertson, C.G.; Hardman, 2021). Yan et al. (2021) found that the surface modification of graphene oxide (GO) nanosheets increased the strength at the break by 90% by showing a positive effect on the cross-link density of nitrile butadiene rubber containing carbon black (N220). Jovanovic et al. (2013) investigated the impact of N330 CB in different proportions on the activation energy, thermal and mechanical stability, properties of acrylonitrile-butadiene/ethylene-propylene-diene (NBR/EPDM) rubber mixtures. While the activation energy of the mix with 70 phr (parts per hundred rubber) CB was found to be the lowest, the best mechanical test results were seen in the NBR/EPDM mixture with 90 phr N330 carbon black added. Among viscoelastic materials, rubber materials have the unique feature of maintaining material integrity even when exposed to high deformation forces; these properties are widely used in energy-absorbing insulators. In a study by Bandyopadhyay et al., the effect of HAF N330 CB amount on the viscoelastic properties of vulcanized natural rubber was investigated. In the study, as the amount of CB increased, the viscoelastic properties of the blends decreased. It caused a decrease in the damping properties of

the vulcanizates with an increase in the amount of CB (Bandyopadhyaya et al. 2022). In a study by Sivaselvi et al., (2020) the effect of different N550 CB amounts on the mechanical properties of the windshield wiper blade was comparatively examined. They found that the mechanical properties of the front wiper blade enhanced with the increase in N550 CB (Sivaselvi et al., (2020) In a study by İsmail et al. (2019) in basic insulator systems, magnetorheological elastomers (MREs) information svstems provide about the performance and other physical properties of the final products by adding N220 carbon black to natural rubber at different rates.

With the realization of the industrial revolution from the discovery of natural rubber to the present, the need for rubber material has increased since the beginning of the 20th century. In addition, Synthetic rubbers such as butadiene rubber (BR), Styrenebutadiene rubber (SBR), acrylonitrilebutadiene rubber (NBR), Chloroprene rubber (CR), Ethylene Propylene Diene rubber (EPDM), Silicone rubber (Q) have begun to be synthesized in industrial scale. Nowadays, different types of rubber are synthesized depending on their purpose and usage areas.

One is Polyepichlorohydrin (PECH), which was synthesized in the 1950s. Polyepichlorohydrin is a polyether with a functional alkyl chloride side group. Epichlorohydrin (ECH) is currently produced using "green" methods, which convert glycerine, a byproduct of biofuel production, into ECH, making it much more environmentally friendly and reducing production costs than traditional synthesis methods (Martin et al.,2016). Due to their unique characteristics, including lowtemperature flexibility and heat and oil resistance, PECH elastomers are utilized in various trading products, such as fuel hoses, gaskets, and air ducts (Ferrier et al.,2021). In the decades between its initial synthesis and the present, PECH and derived materials from PECH have been used for cost, functionality, chemically robust and pliable ether backbone, inexpensive polymer electrolytes (Hu et al., 2015), gas separation (Tu et al., 2021), ion exchange membranes (Tuan et al., 2020) and cold climate performances (Sokolova et al., 2019).

The flexible ether backbone of epichlorohydrin rubber allows for cold-climate applications. Zeon Chemicals L.P. (USA) developed the product code Hydrin T6000, which has the lowest glass transition temperature (Tgt = -60 °C) for use in cold climates or frost-resistant rubber based on epichlorohydrin. Haldeeva et al. (2019) prepared Hydrin T6000 elastomer and N774 and N550 carbon black blends at different ratios and investigated the effect of CB type and amount on residual deformation and mechanical properties. They found that the blend containing 65 phr N774 carbon black best maintained elastic properties. Bukowski et al. found that multi-walled carbon nanotubes (CNTs) at the rate of 1-2% w/w to be added to the hydrin elastomer increase the abrasion resistance (Bukovskiy et al.,2019) In the study of Fedorova et al., (2021) viscoelastic properties of hydrin elastomer containing two different accelerator systems, such as thiuram and guanidine containing N550 carbon black, were investigated. In a similar study, Davydova et al. showed that the cooking system is a prominent parameter in determining the mechanical and physical properties of the hydrin elastomer (Davydova et al., 2021).

This study was carried out to determine the effect of carbon black size on the vulcanization kinetics and mechanical properties of epichlorohydrin rubber blends. For this aim, blends were prepared with the same amount of carbon blacks in different sizes (N220, N330, and N550). The effects of carbon black on the curing characteristics were investigated. However, the effects of the size of the carbon black on the curing kinetics and activation energy of the Poly(epichlorohydrin) elastomer were investigated with the 1st and nthorder kinetic models. Finally, it aims to examine the effects of the test samples prepared from each mixture on Shore A hardness values, compression set, rebound resilience, and tensile strength properties.

#### **2. EXPERIMENTAL SECTION**

#### 2.1. Materials

Polv(epichlorohydrin)(CO) homopolymer, trade name H55, was obtained from Zeon Co. (USA). The H55 has a homopolymer of Epichlorohydrin (ECH) polymers. The Mooney viscosity value of polymers is (@100 °C ML (1 + 4)) and a viscosity range of 50-60, and the monomer content of the homopolymer is 100% epichlorohydrin (ECH). The relative density of H55 is 1.37 g/cm<sup>3,</sup> and the chlorine content is 36% by weight. Carbon blacks (HAF N220/330/550) used as filler were supplied from Omsk Carbon Group (Russia). The particle size of N220 carbon black ranges from 20 to 25 nm. N330 from 28 to 36 nm. and N550 from 39 to 55 nm. Their respective average surface areas are 112-115 m<sup>2</sup>/g, 76-80 m<sup>2</sup>/g, and 39-41 m<sup>2</sup>/g. The vulcanization system was based on ethylene thiourea (Zisnet F-PT) and Diphenyl Guanidine (DPG). Other ingredients are commercial chemicals commonly used in the rubber and tire industry.

#### 2.2. Preparation of Blends

**Table 1** presents the component ratios of the mixtures, expressed in phr. All blends were prepared at 40 °C at 50 rpm/min for 20 minutes using a laboratory two-roll mixing mill.

Component	H55	H55-220	H55-330	H55-550
H55	100	100	100	100
N220	0	40	0	0
N330	0	0	40	0
N550	0	0	0	40
Naphtenic oil Octopus N418	5	5	5	5
Alkylphenol resin	20	20	20	20
6PPD, N-(1,3-Dimethylbutyl)-	1	1	1	1
N'phenyl-p-phenylenediamine Magnesium oxide (MgO)	3	3	3	3
Stearic Acid	1	1	1	1
DPG, N, N'- Diphenylguanidine	0.5	0.5	0.5	0.5
TTCA(TMT), Zisnet 2,4,6- Trimercapto-s-triazine (Trithiocyanuric acid)	0.8	0.8	0.8	0.8
TDQ, 2,2,4 - trimethyl - 1,2 - dihydroquinoline	1	1	1	1

Table 1.	Formulations	of the H55/CB	compounds.
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2.3. Cure Characteristics and Swelling Study

The optimal cure time and curing parameters of blends were determined using a moving die rheometer (Alpha 2000 MDR) at 170/180/190/200 °C according to **ASTM D5289-12**. Tests were

carried out by taking three samples from 3 different points of each blend series.

The crosslinking density of rubber often affects swelling in that it can absorb more solvent molecules due to the less dense crosslink density. Conversely, higher crosslink densities make polymer chains complex to flexibility; for this reason, it reduces chain gaps and restricts solvent molecule absorption into the networks (Darko, 2022) The swell ratio, the greatest equilibrium swelling condition attained during the soaking of the solvent molecules, may be calculated via the swelling technique (Kraus, 1957, Poller et al., 1962) This approach measures the swelling ratio by monitoring swelling polymers' volume or weight increase until swelling equilibrium is achieved (Liu et al., 2020). In this study, the swelling ratio was defined as follows:

$$Q = \left[\frac{(W_s - W_d)}{W_d}\right] \times 100\% \qquad \text{(Eq. 1)}$$

where; The weights of the dry specimen are represented by wd and the swollen specimen by ws, respectively. Rubber samples of a specific weight were soaked in toluene at room temperature for seven days to test for swelling.

#### 2.4. Mechanical Properties of H55/CB Series Elastomers

For all the compounds' optimum cure times, vulcanization was carried out in a pressurized hot press (Brabender) at 200 °C.

**Shore A** hardness was measured according to ASTM D 2240 standard. Hardness values were calculated using a Westop brand Type A durometer (Nishi Tokyo Seimitsu, Japan) by preparing eight samples from 6 mm thick and 16 mm diameter smooth surface samples.

The rebound values of each elastomer were measured using 12.5 mm thick and 30 mm diameter samples with smooth surfaces. The samples were measured using the ZwickRoell 5109 Rebound Resilience Tester (Zwick Roell, Germany). Rebound resilience measurements were taken from 4 samples from each elastomer batch prepared according to ASTM D7121 standard.

The Compression Set was measured according to the ASTM D395 standard. Permanent deformation tests are performed using five 6 mm thick and 16 mm diameter smooth surface samples. The samples exposed to 25% compression for 22 hours were removed from the test setup, and measurements were taken after they were relaxed for 30 minutes.

The tensile properties of the H55/CB blend vulcanizates were measured with a universal test tensile test machine (UTM, Zwick Z010, by Zwick/Roell, Germany) according to ASTM D412, in the 0.5-2.5% elongation zone with a mechanical extensometer at 100 mm/min and the rest of the test at 500mm/min. Eight samples were tested from each batch of blends. The tensile properties are given with deviation values.

### 3. RESULTS AND DISCUSSION

# **3.1.** Cure characteristic and kinetic study of H55/CB blends

The size of the carbon blacks employed makes the most difference in the blends made according to the formula listed in **Table 1.** Curing curves of H55/CB series compounds at different temperatures are given in Figure 1 below. In addition, the measured curing parameters are given in **Table 2**.

As seen in **Figure 1**, the curing curves increase with the addition of carbon black at each temperature value, regardless of the carbon black size.

As the torque increases by two units over the minimum torque during the cure period, scorch time ts<sub>2</sub> is recorded. Scorch occurs when the rubber partially vulcanizes before the product is completely shaped and prepared for vulcanization (Al-Nesrawy et al.,2016). Even at 170 °C, the ts<sub>2</sub> value was not observed during the 20 minutes of curing of the H55 blend, which does not contain carbon black. However, ts<sub>2</sub> values of mixtures containing CB were observed at 170 °C. The lowest ts<sub>2</sub> value was observed in the mixture of H55-**N330** with a value of 2.75±0.01 minutes. This study shows that CB positively affects curing at the lowest temperature value of 170 °C. It was observed that ts<sub>2</sub> and t<sub>90</sub> times of all CB mixtures were shortened.

Even at 170 °C, the ts<sub>2</sub> value was not observed during the 20 minutes of curing of the H55 blend, which does not contain carbon black. However, ts<sub>2</sub> values of mixtures containing CB were observed at 170 °C. The lowest ts<sub>2</sub> value was observed in the mixture of H55-N330 with a value of 2.75±0.01 minutes. This study shows that CB positively affects curing at the lowest temperature value of 170 °C. It was observed that ts<sub>2</sub> and t<sub>90</sub> times of all CB mixtures were shortened. In addition,  $\Delta$ torque values were higher than the reference blend H55. The delta torque value is directly proportional to the crosslink density. Regardless of the size structure of all mixtures containing CB, the ∆torque value at all temperatures was approximately 2/2.5 times higher than the  $\Delta$ torque value of the H55 mixture without CB. As expected, the curing rate increases with the increase in temperature for all mixtures with CRI values. As illustrated in Figure 1 and Table 2, CB-containing been poly (epichlorohydrin) blends have demonstrated to enhance crosslinking reactions and promote crosslink formation. Carbon black improves the vulcanization process by acting as a reinforcing filler that aids in better heat dissipation and speeds up the curing reaction. It is thought to lead to more efficient and faster curing by mitigating side reactions such as transfer and rearrangement reactions that would otherwise compete with crosslinking.

Temperature	Compound Code	ts₂ (m)	t <sub>90</sub> (m)	ΔTork (dNm)	CRI(m <sup>-1</sup> )
	H55	$0.00 \pm 0.00$	$16.40 \pm 0.05$	$1.82 \pm 0.01$	$6.10 \pm 0.02$
170	H55-N220	3.33±0.06	14.81±0.09	6.18±0.12	8.71±0.03
ů ů	H55-N330	2.75±0.01	$14.70 \pm 0.01$	6.67±0.01	8.37±0.01
	H55-N550	4.30±0.03	$15.58 \pm 0.06$	$5.09 \pm 0.01$	8.87±0.03
	H55	13.42±0.08	$15.30 \pm 0.10$	2.36±0.00	53.48±0.40
180	H55-N220	2.09±0.01	12.87±0.04	7.03±0.01	9.28±0.02
ů ů	H55-N330	$1.70 \pm 0.00$	$12.94 \pm 0.01$	7.61±0.04	$8.90 \pm 0.01$
	H55-N550	2.64±0.15	14.07±0.12	$5.98 \pm 0.16$	8.75±0.02
	H55	8.13±0.20	13.16±0.04	2.67±0.03	$19.91 \pm 0.64$
19(	H55-N220	1.43±0.04	10.38±0.17	7.33±0.01	$11.17 \pm 0.17$
ů ů	H55-N330	$1.16 \pm 0.02$	$10.29 \pm 0.11$	7.88±0.23	$10.95 \pm 0.15$
	H55-N550	$1.65 \pm 0.02$	$11.80 \pm 0.13$	6.60±0.03	9.85±0.10
° 20	H55	5.05±0.03	8.85±0.01	2.73±0.01	26.32±0.29
~ ° 8	H55-N220	$1.03 \pm 0.01$	$7.09 \pm 0.01$	7.26±0.00	$16.49 \pm 0.02$
	H55-N330	0.83±0.00	2.21±0.00	7.87±0.02	16.14±0.02
	H55-N550	$1.15 \pm 0.00$	2.64±0.01	6.58±0.02	13.98±0.04

Table 2. Cure values of H55, H55 N220, H55 N330 and H55 N550 blends.



Figure 1. Curing curves of H55 (a), H55 N220 (b), H55 N330(c), and H55 N550 (d) Blends at 170 °C, 180 °C, 190 °C, and 200 °C.

The Cure Rate Index (CRI) is a parameter used in rubber and elastomer processing to quantify the rate of vulcanization or curing. It indicates how quickly a rubber compound transitions from uncured to fully cured when subjected to heat and curing agents (such as peroxides or sulfur-based systems). The cure index (CRI) indicating the cure rate of the blends is defined in **Equation 2.** 

$$CRI = \frac{100}{(t_{90} - t_{s2})}$$
 (Eq. 2)

To analyze the curing kinetics of the prepared H55-CB blends,  $\alpha$ -time graphs were generated using **Equation 3** based on the curing curve data for all blends. The  $\alpha$ -time plots for these blends are presented in **Figure 2**. Furthermore, to determine the cure rate content and activation energy of elastomers according to the first-order kinetic model, the state of cure ( $\alpha$ ) values were calculated by evaluating the cure curves of ECHR-CB blends at four different temperatures using Equation 3.

$$\alpha(t) = \frac{Mt - ML}{MH - ML}$$
 (Eq. 3)

where MH is the maximum torque, ML is the minimum torque, and Mt is the torque at the time. k values were calculated according to the first-order kinetic model using **Equation 4** by evaluating the area between  $\alpha$ =0.25-0.45 in the cure curve.

$$\ln(\alpha) = k(T) \times t$$
 (Eq. 4)

Activation energies of elastomers have been calculated with k values obtained at different temperatures using the Arrhenius equation.

$$K = k_0 \exp(-Ea/RT)$$
 (Eq. 5)

Ea is the activation energy, R is the universal gas constant, and T is the absolute temperature.



Figure 2.  $\alpha$ -time curves of H55, H55 N220, H55 N330, and H55 N550 blends at 150 °C, 160 °C, 170 °C, and 180 °C.

**Figure 2** shows the state of cure ( $\alpha$ ) values versus cure time of H55 series compounds curves. The region between  $\alpha$ =0.25-0.45 in the  $\alpha$ -time curve was evaluated to calculate k values according to the first-order kinetic model using **Equation 4**.

The cure rate was calculated using the slope of the ln $\alpha$ -time curves of the blends of H55, H55-N220, H55-N330, and H55-550 used to evaluate the (k) value of the content.



Figure 3. Ina-time curves of H55, H55 N220, H55 N330, and H55 N550 blends.

Figure 4 gives the ln k versus (1/T) of H55, H55-N220, H55-N330, and H55-N550 blends from the Arrhenius equation at 170  $^{\circ}$ C, 180  $^{\circ}$ C, 190  $^{\circ}$ C, and 200  $^{\circ}$ C.



**Figure 4.** 1<sup>st</sup> order cure kinetics; In k versus (1/T) of H55, H55 N220, H55 N330, and H55 N550 blends from Arrhenius equation, at 170 °C, 180 °C, 190 °C, and 200 °C.

Then, using **Equation 5**, the activation energies of each mixture were found. **Tables 3** and **4** present

the cure rate content and activation energy of H55 elastomers.

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1 <sup>st</sup> order "k" values						
Temp (°C)	H55	H55-N220	H55-N330	H55-N550		
170	0.178±0.00 5	0.272±0.008	0.321±0.010	0.221±0.007		
180	0.248±0.00 7	0.413±0.012	0.424±0.017	0.320±0.010		
190	0.360±0.01 1	0.608±0.012	0.617±0.019	0.505±0.025		
200	0.568±0.01 7	0.771±0.023	1.007±0.022	0.728±0.022		

Table 3. First order kinetic model; Cure rate content of H55 N220, H55 N330 and H55 N550.

 Table 4. Activation energy of H55 N220, H55 N330 and H55 N550 blends.

Blend Code	Ea (kJ/mol )
H55	67.13±3.36
H55 N220	61.30±4.29
H55 N330	66.09±2.64
H55 N550	70.35±3.52

According to the first-order kinetic model of the cure curves of the H55-CB series elastomer, **k** values increased with temperature. As seen in **Table 3**, the k value increased with the use of CB, and this increase was more pronounced at high temperatures. The rise in the k constant with the use of CB is that CB prevents reactions other than crosslinking, such as transfer and rearrangement, which compete with the cross-linking reaction. The highest k-constant value is seen in the **H55-N330** coded blend, while the lowest k-constant value is in the **H55** coded blend. When the Ea values were examined, it was seen that the highest activation energy value was in the **H55-N550** coded blend.

For nth-order curing kinetics, the  $\alpha$ -time curves of the mixtures at different temperatures were iteratively fitted to the curing curves using **Equation 6**. The nth-order kinetic model serves as the second method for calculating the reaction rate constant (k), activation energy (Ea), and reaction order (n). To determine the values of k and n, the state-of-cure time curves were analyzed

using the OriginLab program based on  $\ensuremath{\textit{Equation}}$  6:

$$\alpha = \frac{k(t-ts)^n}{1+k(t-ts)^n}$$
 (Eq. 6)

Where,  $t_s$  is scorch time.

**Equation 5** was then used to calculate the activation energies of the elastomers. **Figure 6** presents the  $\alpha$ -time curves for the H55, H55-N220, H55-N330, and H55-N550 blends. According to **Equation 5**, the reaction rate constants (k) and reaction order (n) for each mixture at different temperatures were determined using the Isayev-Deng model (Isayev et al.,2009; Farid et al., 2007, Mansilla et al., 2006), applying a scientific graphing program and nonlinear curve fitting. The reaction rate constants (k) and reaction order (n) for the H55, H55-N220, H55-N330, and H55-N550 blends are summarized in **Tables 5** and **6**.



Figure 6.  $\alpha$ -time curves of H55, H55 N220, H55 N330 and H55 N550 a with curve fitting at 200 °C.



**Figure 7.** nth order cure kinetics; In k versus (1/T) of H55, H55 N220, H55 N330, and H55 N550 blends from Arrhenius equation, at 170 °C, 180 °C, 190 °C, and 200 °C.

According to the n<sup>th</sup> kinetic model of the cure curves of H55-CB blends, When the k values were examined, it was seen that the value of the k rate constant increased with the increase in temperature for all blends. The highest k value was seen in the **H55-N330** coded blend, as in the first-order kinetic model, while the lowest k value was seen in the **H55** coded blend. When the Ea values were examined, it was seen that the highest activation energy value was in the **H55coded** blend. Carbon black interacts with curing agents such as sulfur and accelerators, modifying the overall kinetics of vulcanization. The type and structure of carbon black affect how it absorbs these chemicals, influencing cure speed and efficiency. Carbon black enhanced the cure rate by suppressing competing reactions, such as transfer and rearrangement, that are distinct from crosslinking reactions. CB plays two roles in the vulcanization kinetics (Razzaghi-Kashani et al., 2018): first, it exhibits a catalytic effect that accelerates the initial reactions among vulcanization agents. Aksüt, D. (2025), JOTCSB, 8(1), 123-136.

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Compd	170 °C		180 °C		190 °C		200 °C	
	k	n	k	n	k	n	k	n
H55	$0.02 \pm 0.02$	$2.22 \pm 0.05$	$0.04 \pm 0.01$	$1.98 \pm 0.04$	$0.09 \pm 0.04$	$1.79 \pm 0.03$	$0.18 \pm 0.03$	$1.76 \pm 0.11$
H55-N220	$0.41 \pm 0.06$	$1.78 \pm 0.03$	$0.15 \pm 0.01$	$1.64 \pm 0.03$	$0.32 \pm 0.01$	$1.43 \pm 0.02$	$0.63 \pm 0.01$	$1.37 \pm 0.02$
H55-N330	$0.09 \pm 0.01$	$1.72 \pm 0.05$	$0.23 \pm 0.01$	$1.41 \pm 0.03$	$0.43 \pm 0.01$	$1.29 \pm 0.02$	$0.80 \pm 0.016$	$1.21 \pm 0.02$
H55-N550	$0.05 \pm 0.01$	$1.84 \pm 0.05$	$0.11 \pm 0.01$	$1.62 \pm 0.04$	$0.23 \pm 0.01$	$1.51 \pm 0.03$	$0.47 \pm 0.01$	$1.41 \pm 0.02$
Table 5.       n order kinetic model: Cure rate content of H55-REF. H55-N220. H55-N330 and H55-550.								

Table 6. Activation energy of H55 N220, H55 N330 and H55 N550 blends.

Blend Code	Ea (kJ/mol)		
H55-REF	146.4±7.3		
H55 N220	131.7±7.9		
H55 N330	128.8±4.5		
H55 N550	130.4±9.1		

Figure 8 below shows a comparative bar graph of activation energy values calculated from 1st—and

nth-order kinetic models of H55, H55-N220, H55-N330, and H55-N550.



Figure 8. Calculated 1<sup>st</sup> and n<sup>th</sup> order activation energy values of H55, H55 N220, H55 N330 and H55 N550.

The 1st-order kinetic model's activation energy values were discovered to be lower than those of the nth-order kinetic model, as shown in **Figure 8**. The activation energy levels of all blends, it was noted, did not significantly differ. This is because only data from  $\alpha$ -time graphs between 0.25 and 0.40 are considered in the first-order kinetic model. With the addition of carbon black, the activation energy value is reduced by around 19% when considering the nth-order kinetic modeling. Carbon black interacts with curing agents such as sulfur and accelerators, modifying the overall kinetics of vulcanization. The type and structure of carbon black affect how it absorbs these chemicals, influencing cure speed and efficiency.

## 3.2. Swelling studies of H55/CB Blends

The swelling ratio is a key indicator of an elastomer's cross-link density and interaction with solvents. A lower swelling ratio suggests higher cross-link density, which restricts the penetration of solvents into the polymer network. The swelling ratios given in Figure 9 show that adding carbon black (CB) to the hydrin elastomer (H55) leads to a decrease in the swelling ratio. While the highest swelling ratio was observed in the blend coded H55 (without CB) with  $3.327 \pm 0.0274$ , the lowest was observed in the blend coded H55-N330 with  $1.466 \pm 0.003$ .



Figure 9. Swelling ratio of H55, H55 N220, H55 N330 and H55 N550 blends.

This phenomenon can be attributed to multiple factors. Carbon black is a reinforcing filler, enhancing mechanical stability and reducing free volume within the polymer matrix. Additionally, it promotes the formation of a highly cross-linked polymer network after curing, further restricting solvent penetration. Consequently, the interaction between polymer chains and the solvent is significantly diminished, reducing the elastomer's solvent absorption capacity. With the addition of carbon black, the free volume within the polymer matrix decreases, leading to a more compact structure. Moreover, rheometer studies indicate an increase in delta torque values, suggesting that carbon black also contributes to an enhanced cross-link density in the elastomer network.

# **3.3.** Mechanical Properties of H55/CB series blends

Shore A hardness, Rebound Resilience, Compression Set, and tensile strength tests were performed to examine the effect of different sizes of carbon black on the mechanical properties of Epochlorohydrin elastomer. Shore A hardness, Compression Set, and Rebound resilience value of Epichlorohydrin Rubber with carbon black in different sizes are given in **Table 7** below.

**Table 7.** Basic Mechanical Properties of Epichlorohydrin Rubber with Carbon Black in Different Sizes.

Blend Code	Shore A	Compression Set	Rebound Resilience
H55	20±1	11.4±5.0	6.8±0.5
H55-N220	60±1	44.9±3.8	6.5±0.6
H55-N330	64±2	47.4±1.0	7.5±0.6
H55-N550	60±1	27.7±2.8	6.0±0.2

With the addition of CB to ECHR, the shore A value of all blends increased approximately twofold. There was no significant difference in Rebound Resilience values in all blends. The compression set values of H55/CB Blends increased with the addition of carbon black.

**Figure 10** provides stress-strain curves for the H55, H55-N220, H55-N330, and H55-N550 coded compounds.



Figure 10. Strain-Stress curves of H55, H55 N220, H55 N330 and H55 N550 coded compound.

The stress-strain curve values of the H55/CB significantly improved the mechanical values of mixtures given in **Table 8** show that adding CB H55.

Blend Code	Emod (MPa)	Emod @ 100% strain (MPa)	Emod @ 300% strain (MPa)	Tensile strength (MPa)	Elongation at break (%)
H55	0.70±0.14	0.34±0.01	$0.78 \pm 0.02$	3.0±0.4	553±26
H55-N220	8.90±1.11	$1.49 \pm 0.11$	3.58±0.16	10.8±0.8	663±22
H55-N330	9.90±1.07	2.12±0.09	5.71±0.25	13.9±0.6	656±34
H55-N550	5.90±0.36	$1.70 \pm 0.11$	5.35±0.49	10.6±0.8	591±56

Table 8. Tension test results of H55, H55-N220, H55-N330 and H55-N550 coded elastomers.

The stress-strain curves in Figure 10 demonstrate that the stiffness of the epichlorohydrin elastomer increases with the addition of carbon black. This trend is further supported by the Shore A hardness test values, which confirm the material's enhanced rigidity. The elastic modulus, an indicator of crosslink density, exhibited an average eightfold increase, irrespective of CB particle size. Additionally, swelling ratios decreased in CBcontaining blends, reinforcing that CB enhances cross-linking and restricts solvent penetration (Bezzazi et al.,2021). Among the tested formulations, the H55-N330 elastomer exhibited the highest proportional increase in elastic modulus, measured at 9.90 ± 1.07 MPa, making it approximately 13 times more elastic than the CBfree H55 elastomer, which had a modulus of 0.70 ± 0.14 MPa. Moreover, modulus values at 100% and 300% elongation indicate that CB significantly properties enhances the mechanical of epichlorohydrin rubber. While there was no substantial difference in elongation at break values, a general increase in elongation at break was observed with incorporating CB, suggesting improved toughness and flexibility.

### 4. CONCLUSION

Adding carbon black (CB) to H55 elastomers improves curing kinetics and mechanical performance. Scorch time (ts2) was reduced, accelerating the onset of vulcanization, while t90 values decreased, leading to a more efficient curing process. The delta torque ( $\Delta T$ ) values increase, suggesting a higher cross-link density, enhancing overall material strength. Mechanical testing confirmed that CB improves stiffness, tensile strength, and modulus of elasticity, with the H55-N330 blend showing the best mechanical performance. Specifically, the elastic modulus increased by up to 13 times, and the swelling ratio decreased by 54%, confirming improved solvent resistance and durability. The activation energy required curing decreased (Ea) for by approximately 15% with CB addition, indicating a more energy-efficient vulcanization process. The Shore A hardness of all CB-filled blends nearly doubled, confirming increased material rigidity. Although no significant differences were observed in elongation at break, the overall toughness and resilience of the elastomer were improved. Among all formulations, H55-N330 exhibited the best balance between cure rate, mechanical strength, and solvent resistance, making it highly suitable for industrial applications requiring enhanced durability and performance. These findings suggest that CB-reinforced H55 elastomers can be effectively utilized in high-performance sealing, automotive, and aerospace applications.

# **5. CONFLICT OF INTEREST**

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### 5. REFERENCES

- A F Fedorova and M L Davydova 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1079** 032046 **DOI** 10.1088/1757-899X/1079/3/032046
- A. Almena, M. Martín,.(2016). Ind. Eng. Chem. Res., 55, 3226. <u>https://pubs.acs.org/doi/10.1021/acs.iecr.5b</u> 02555
- Ajay K. Manna, A.K. Bhattacharyya, P.P. De, D.K. Tripathy, S.K. De, Dennis G. Peiffer. (1998).Effect of silane coupling agent on the chemorheological behaviour of epoxidised natural rubber filled with precipitated silica, Polymer, Volume 39, Issue 26, Pages 7113-7117. <u>https://doi.org/10.1016/S0032-3861(98)00155-4</u>.
- Al-Nesrawy, Sameer Hassan Hadi, Mohammed H. Al-maamori and Hamad Rahman Jappor. (2016).Effect of Temperature on Rheological Properties of SBR Compounds Reinforced by some Industrial Scraps as a Filler. international journal of chemical sciences 14: https://doi.org/10.1088/1742-6596/1973/1/012161.
- Arrillaga A, Zaldua AM, Atxurra RM, Farid AS. (2007). Techniques used for determining cure kinetics of rubber compound. Eur Polym J.; 43:4783-99. https://doi.org/10.1016/j.eurpolymj.2007.08. 024
- Bandyopadhyaya, S.; Kitey, R.; Upadhyay, C.S., (2022).The Effect of Carbon Black Content on Viscoelastic Properties of Vulcanized Natural Rubber.,Phys. Sci. Forum 2022, 4, 9. https://doi.org/10.3390/psf2022004009

Boukfessa, H., & Bezzazi, B. (2021). The effect of carbon black on the curing and mechanical properties of natural rubber/ acrylonitrile- butadiene rubber composites. *Journal of Applied Research and Technology*, 19(3), 194–201. <u>https://doi.org/10.22201/icat.24486736e.202</u> <u>1.19.3.168</u>

- Buckley DJ, Berger M, Poller D (1962) The swelling of polymer systems in solvents. I. Method for obtaining complete swelling-time curves. J Polym Sci 56:163-174. https://doi.org/10.1002/pol.1962.120561631 5
- Bukovskiy, P.O., Morozov, A.V., Petrova, N.N. et al.(2019). Study on the Influence of Activated Carbon Nanotubes on the Tribological Properties of Frost-Resistant Rubber. Mech. Solids 54, 1250–1255.

https://doi.org/10.3103/S002565441908015 6

- Chu HZ, Liu D, Cui ZW, Wang K, Qiu GX, Liu GY (2020) Effect of crosslink density on solubility parameters of styrene butadiene rubber and the application in pre-screening of new potential additives. Polym Testing 81:106253. https://doi.org/10.1016/j.polymertesting.201 9.106253
- Darko, C. (2022). The link between swelling ratios and physical properties of EPDM rubber compound having different oil amounts. J Polym Res 29, 325. https://doi.org/10.1007/s10965-022-03179-z
- Davydova, M.L., Shadrinov, N.V., Khaldeeva, A.R. et al.(2021) Influence of Vulcanizing System on Properties and Structure of Rubbers Based on Hydrin T6000 Epichlorohydrin Rubber. *Inorg. Mater. Appl. Res.* 12, 859-865. https://doi.org/10.1134/S207511332104011 0
- Geetanjali Shukla, Robert C. Ferrier Jr.(2021). The versatile, functional polyether, polyepichlorohydrin: History, synthesis, and applications, J Polym Sci. 2021; 59:2704– 2718. <u>https://doi.org/10.1002/pol.20210514</u>
- H. Hu, W. Yuan, Z. Jia, G. L. Baker. (2015). Ionic liquid-based random copolymers: a new type of polymer electrolyte with low glass transition temperature, RSC Adv. 2015, 5, 3135. <u>https://doi.org/10.1039/C4RA13432</u>]
- Haldeeva AR, Davydova ML, Sokolova MD. (2019). Development of Frost-Resistant Rubber Based on Epichlorohydrin Rubber of Hydrin T6000 Brand. MSF 2019; 945:356-61. https://doi.org/10.4028/www.scientific.net/m sf.945.356.
- Ismail, H., Rusli, A., Rashid, A.A., 2005. Maleated natural rubber as a coupling agent for paper sludge filled natural rubber composites. Polymer Testing, 24(7): 856-862. DOI: 10.1016/j.polymertesting.2005.06.011
- Jovanovic. V., Budinski. S., Samardzija. J., Gordana. M., Marinovic. C., The influence of carbon black on curing kinetics and thermal aging of acrylonitrile-butadiene rubber, Chemical Industry & Chemical Engineering Quarterly, 2009, 15(4):283-289
- Jun Qiu, Hongfei Wang, Jingwen Shao, Kefu Zhang, Juan Wu, Lifeng Yan.(2021). S4-Containing hyperbranched polymer modified graphene oxide as strong linker for both rubber and carbon black to enhance the

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crosslinking and mechanical properties of nitrile butadiene Rubber. Chemical Engineering Journal 417, 129336. https://doi.org/10.1016/j.cej.2021.129336

- Kashani M. R.-., Hosseini S. M., Catalytic and networking effects of carbon black on the kinetics and conversion of sulfur vulcanization in styrene butadiene rubber.Soft Matter, 2018,14, 9194. DOI: 10.1039/c8sm01953c
- Karnda Sengloyluan, Kannika Sahakaro, Wilma K. Dierkes, Jacques W.M. Noordermeer, "Silica-reinforced tire tread compounds compatibilized by using epoxidized natural Rubber", European Polymer Journal 51 (2014) 69-79, http://dx.doi.org/10.1016/j.eurpolymj.2013.1 2.010
- Kraus G (1957) Degree of cure in fillerreinforced vulcanizates by the swelling method. Rubber Chem Technol 30:928-951. https://doi.org/10.5254/1.3542738
- Mark, J. E.; Erman, B.; Eirich, F. R. (1994). Science and Technology of Rubber, 2nd ed.; Academic Press: New York, p 388.
- Marzocca AJ, Mansilla MA.(2006). Vulcanization kinetic of styrene-butadiene rubber by sulfur/TBBS. J Appl Polym Sci.;101: 35-41. https://doi.org/10.1002/app.23173
- R. Ismail, Nurul Husna Binti Rajhan, Hanizah Abdul Hamid, Azmi Ibrahim.(2019).
   "Experimental data for effect of carbon black loading on tensile, hardness and rebound of magnetic iron filled natural rubber composites.", Data in brief 25, 104166. https://doi.org/10.1016/j.dib.2019.104166
- Robertson, C.G.; Hardman, N.J. (2021). Nature of Carbon Black Reinforcement of Rubber: Perspective on the Original Polymer Nanocomposite. Polymers, 13, 538. https://doi.org/10.3390/polym13040538
- Schaal, S.; Coran, A. Y.; Mowdood, S. K.(2000). The effects of certain recipe ingredients and mixing sequence on the rheology and processability of silica- and carbon blackfilled tire compounds, *Rubber Chem. Technol.* 2000, *73*, 240. https://doi.org/10.5254/1.3547588
- Sivaselvi K., Kandasamy Gopa,(2020). Study to enhance the mechanical properties of natural rubber by using the carbon black (N550). Materials Today: Proceedings, Volume 26, Part 2, Pages 378-381. https://doi.org/10.1016/j.matpr.2019.12.059

- Sokolova, M. D., Fedorova, A. F., & Pavlova, V. V. (2019). Research of Influence of Plasticizers on the Low-Temperature and Mechanical Properties of Rubbers. Materials Science Forum, 945, 459-464. https://doi.org/10.4028/www.scientific.net/m sf.945.459
- Tuan, C. M., Cong Tinh, V. D., & Kim, D. (2020). Anion Exchange Membranes Prepared from Ouaternized Polyepichlorohydrin Cross-Linked 1-(3-aminopropyl)imidazole with Grafted Poly(arylene ether ketone) for Enhancement Toughness of and Conductivity. Membranes, 10(7), 138. https://doi.org/10.3390/membranes1007013 8
- Vojislav Jovanovic´, Suzana Samarzčija-Jovanovic´, Jaroslava Budinski-Simendic´, Gordana Markovic´, Milena Marinovic´-Cincovic´, Filler in Rubber Industry Silica and CB which purpouse they uses in Rubber industry", Composites: Part B 45 (2013) 333-340, <u>http://dx.doi.org/10.1016/j.compositesb.201</u> 2.05.020
- X. Sun, A.I. Isayev.(2009). Cure kinetics study of unfilled and carbon black filled synthetic isoprene rubber, Rubber Chemistry and Technology 82 (2) 149-169. <u>https://doi.org/10.5254/1.3548241</u>
- Yimin Zhang, S. Ge, B. Tang, T. Koga, M. H. Rafailovich, J. C. Sokolov, D. G. Peiffer, Z. Li, A. J. Dias, K. O. McElrath, M. Y. Lin, S. K. Satija,S. G. Urquhart, H. Ade and D. Nguyen, (2001). Effect of Carbon Black and Silica Fillers in Elastomer Blends, *Macromolecules*, 34, 7056-7065. https://doi.org/10.1021/ma010183p
- Yiran Fan a, b, Geoff D. Fowler b, Ming Zhao. (2020). The past, present and future of carbon black as a rubber reinforcing filler e A review. Journal of Cleaner Production 247 119115. https://doi.org/10.1016/j.jclepro.2019.11911 5
- Zhuoheng Tu, Mingzhen Shi, Xiaomin Zhang, Pingping Liu, Youting Wu, Xingbang Hu. (2021). Selective membrane separation of CO2 using novel epichlorohydrin-aminebased crosslinked protic ionic liquids: Crosslinking mechanism and enhanced salting-out effect. Journal of CO2 Utilization, Volume 46, 2021. https://doi.org/10.1016/j.jcou.2021.101473.