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EFFECT OF METAL DOPED ZSM-5 CATALYST ON AROMATIC YIELD AND COKE FORMATION IN MICROALGAL BIO-OIL PRODUCTION

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Abstract

It has been known that synthetic zeolites as a cracking catalyst can increase aromatic hydrocarbon amount by providing deoxygenation of pyrolytic bio-oil. However, deactivation of zeolite because of coke deposition has been a serious problem. In this study, Ni and Co metals which was impregnated to ZSM-5 were used as catalyst for co-pyrolysis of *Spirulina*–Polystyrene and *Spirulina*-Polyethylene. The yields of bio-oils were compared to each other. The bio-oils which formed from catalytic co-pyrolysis were analyzed via GC-MS. Amounts of target aromatic compounds which were benzene, o-xylene, naphthalene in the bio-oils were determined. Coke amounts on the catalysts were computed. Regarding coke deposition (11%) and bio-oil yield (55%), it was determined that Ni-ZSM-5 was an effective catalyst for co-pyrolysis Polystyrene and *Spirulina*. For *Spirulina* and Polyethylene, it was obtained that bio-oil yield and coke deposition were 50% and 14% for Ni-ZSM-5.

Key Words: Bio-oil, ZSM-5, metal impregnation, GC-MS, green chemical production

1. Introduction

Synthetic zeolites as an important microporous crystalline material, have been used in industrial catalytic applications (Kakiuchi et al., 2019). Researchers have made modifications on synthesis methods of synthetic zeolites. In this way, it can be possible to change property and structure of synthetic zeolites (Peng et al., 2019). Framework of a zeolite is composed of iterative cornered units. These units occur from connection of SiO4 and AlO4 compounds to each others in a specific rate and geometry. Si/Al ratio in the unit have to bigger than 1. Each zeolite has different framework structure and pore size because of different geometries of that units. Pore size of zeolites generally are not under 1 nm. There are 230 different zeolites with respect to framework structure. Si/Al ratio of each zeolite can be varied in a framework structure. The most using zeolite types in industrial catalytic applications can be classified as MFI (H-ZSM-5 etc.), BEA (Zeolite Beta etc.), MOR (Mordenite etc.), FAU (Zeolite Y etc.) and FER (Ferrierite etc.). These zeolites have been utilized especially in petrochemicals production which are aromatic hydrocarbons like gasoline, propylene, ethylbenzene and cumene. Each of them have different physical and chemical properties however some desired features are mutual for them such as high density because of the strong oxygen bond between Si and Al and thermal stability up to 800 ºC (Fan & Jiao, 2019).

Nowadays, it has been known that fossil fuel using causes climate change. Therefore, researchers have widely worked on reducing fossil fuel addiction (Choo et al., 2020). So, these well-known zeolites can be used in renewable energy applications such as biomass conversion (Iisa et al., 2020), fuel cells (Nagar et al., 2019), removing volatile organic carbons (formaldehite etc.) (Suárez et al., 2019) and NOx gases (Khivantsev et al., 2019), water purification (Fanta et al., 2019; Özçakir, 2020) as well. Researchers have believed that the zeolites are important to produce renewable fuels (Cao et al., 2020) and green chemicals (Liu et al., 2019). Zeolites as a cracking catalyst can increase biofuel quality by providing deoxygenation of pyrolytic bio-oil (Ibarra et al., 2019). Moreover, zeolites can be used in catalytic cracking of plastic wastes to produce invaluable chemicals by providing depolymerization of pyrolytic liquid (Lin et al., 2019).

However, deactivation of zeolite because of coke deposition has been a serious problem for both biofuel and chemical production (Hita et al., 2019). There have been several ways to prevent coke deposition on zeolite. One of them is changing Si/Al ratio of zeolite (Eschenbacher et al., 2020). Adding mesoporouses in the structure and metal doping form another ways (Srivastava et al., 2006; Gurdeep Singh et al., 2020). It has been known that obtaining hierarchical structure can change the zeolite acidity (Palizdar & Sadrameli, 2020). Besides that, aromatic

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yield can not change in bio-oil on that way. And, coke deposition can increase because of large mono-aromatics on the catalyst surface by using that route. High acidity, low Si/Al i.e., can lead to decrease oxygen amount and to increase aromatic amount in bio-oil. Besides that, it can prevent coke deposition on catalyst. Metal doping on zeolites, includes two steps. Firstly, proton takes the place of cation in zeolite. Then, metal impregnation on zeolite occurs. In that way, the metal forms active sites on to the zeolite (Serrano et al., 2018).

In literature, many research was found about the effect of metal doping on zeolite for coke minimization. Li et al. (2020) recorded with metal loading on ZSM-5 bio-oil yield decreased. However, they said that Fe and Co metal doping increased Mono Aromatic Hydrocarbon (MAH) yield 2.5 times. Besides that, they determined that Fe doping decreased coke content significantly (Li et al., 2020). Zheng et al. (2017) determined that Ga, Zn, Ni, Co, Mg or Cu doping on ZSM-5 increased gas yield, while it decrased liquid yield. They obtained maximum bio-oil yield and minimum coke deposition as 26% and 22% respectively for Ga-ZSM-5 between metal doped catalysts. Also, they concluded that Co-based catalyst increased indene formation, however Ni-based catalyst increased benzene formation (Zheng et al., 2017). Du et al. (2013) recorded that Zeolite Y and ZSM-5 gave the positive results for aromatic production in bio-oil. They declared that the most suitable Si/Al ratio was 80 to maintain aromatic yield at the highest level and coke at the minimum. They obtained that Cu and Ga doping on catalyst which had that ratio increased aromatic yield (Du et al., 2013). However, some researches in the literature have defended the opposite opinion on the metal doping effect. For example, Persson et al. (2019) determined that Fe or Ni loading on ZSM-5 led to form coke on catalyst. They determined that Ni or Fe loading on ZSM-5 increased MAH yield. Ni-ZSM-5 increased naphtalene yield also (Persson et al., 2019).

It has been known that *Spirulina* (SP) as a kind of microalgae can be cultivated barren fields, wastewater with fast growth rate. It has high protein content (74 %). During its pyrolysis, proteins degrade to nitrogenous and oxygenated components in bio-oil. When ZSM-5 is used in its pyrolysis, these components convert to aromatic compounds (Chagas et al., 2016). It has been known that plastics has high hydrogen content. Thus, they increase bio-oil yield in co-pyrolytic studies. In addition, it has been thought that plastics improved aromatic compounds in bio-oil (Elsayed & Eseyin, 2016).

Among the other metals, Ni and Co promote deoxygenation reaction more efficiently, reduce coke formation and increase aromatic hydrocarbon yield (Zheng et al., 2017). Thus, in this study, Ni and Co metals were impregnated to ZSM-5. H form, Ni and Co loaded form of ZSM-5 were synthesized. For catalytic testing, co-pyrolysis of SP and Polystyrene (PS), SP and Low Density Polyethylene (LDPE) were carried out. Yields of target aromatic compounds were determined via Gas Chromatography-Mass Spectrometry (GC-MS). Coke amounts on the catalysts were compared to each other.

2. Materials and Methods

2.1. Materials

Spirulina sp. Microalgae in powder form was bought from a local herbalist. Its elemental analysis and particle size were described in our previous research (Özçakır & Karaduman, 2019). According to the results , average particle size of the sample was detected 37 µm. Specific surface area was detected as 0.468 m2/g. Also, it was detected that *Spirulina* had carbon content nearly 50% by mass.

PS foam was provided from a hospital as a blood collection tube tray in the form of waste. It was sliced to small fragments. Then, its air was removed in furnace at 125 ºC during 4 hours. LDPE whose type of F2-12 was provided from Petkim Petrokimya Holding A.Ş.

ZSM-5 powder in ammonium form was purchased from Zeolyst International. Ni(NO3)2.6H2O and Co(NO3)2·6H2O were supplied from Acros Organics and Surechem Products.

2.2 Catalyst Synthesis

Catalytic co-pyrolysis was done with three type catalysts which were H-ZSM-5, Ni-ZSM-5 and Co-ZSM-5. In catalyst synthesis, the study of Güleç et al. was applied (Güleç et al., 2018). For Ni-ZSM-5 and Co-ZSM-5, metal was doped 10% of total mass. The steps for metal doping were summarized in Fig 1. Calcination was made in Nabertherm GmbH brand and LV 5/11/P320 model furnace. According to calcination program which was shown in Fig 2, 550 ºC was chosen to remove ammonium in commercial form of ZSM-5. H-ZSM-5 powder after

calcination was pressed under 10 tonnes to obtain the form of pellet. Ni and Co doping to H-ZSM-5 were made by using wet impregnation method. To obtain Ni-ZSM-5 which had 10% by mass Ni, adequate amount of Ni(NO3)2.6H2O was weighed and mixed with H-ZSM-5. After 20 mL pure water adding to that mixture, the solution was obtained by dispersing in ultrasonic bath whose model was Elma T310. Then, the solution was held at room temperature during 24 hours. After then, the solution which became slurry form was dried at 120 ºC during 4 hours. Lastly, the calcination program was used again. 350 ºC in calcination program was chosen for nitrate removing in the metal salt. To obtain Co-ZSM-5 which had 10% by mass Co, the same route was applied. Brunauer-Emmett-Teller (BET), Scanning Electron Microscope (SEM) and X-ray fluorescence (XRF) analysis of the catalysts were given in the previous research (Özçakır & Karaduman, 2019). According to BET analysis, it was determined that surface area and total pore volume of H-ZSM-5 were 280 m2g-1 and 0.263 cm3g-1. However, loading metals to the zeolite was reduced surface area and total pore volume compared to the non-doped one. In addition to that, it was found that whole catalysts belonged to microporous class with respect to average pore size (2 nm). According to SEM analysis, it can be understood appearently that there are no important difference between the morphology of metal loaded ones and non-loaded one. According to XRF analysis, it was calculated that Si/Al molar ratio of all catalysts was in the range between 60 and 70. Besides that, it was confirmed that the desired ratio of metal loading on the catalysts was reached.

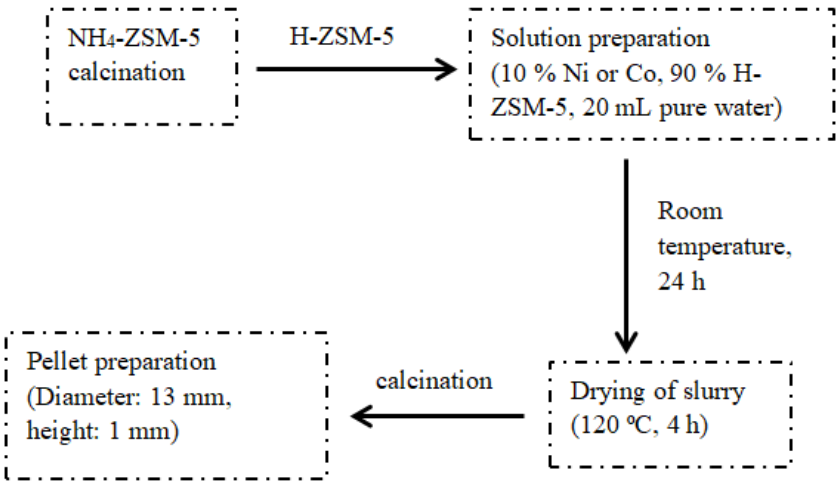


Figure 1. Catalyst preparation steps.

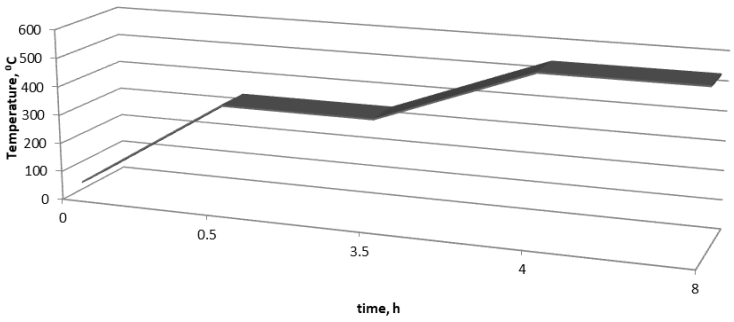


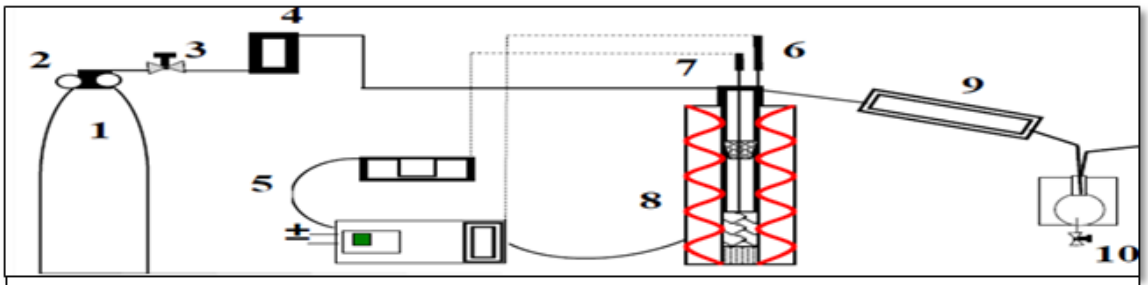
Figure 2. Calcination programme.

2.3 Catalytic Testing

All glass equipment and feedstock were weighed via Shimadzu UX420H brand analytical balance before the experiments. Whole runs were carried out 15 g of feed, 25 mL/min Nitrogen flow, 10 ºC/min heating rate. For catalytic runs, catalyst bed in the middle of reactor was used to put the catalyst pellets. Glass equipments were linked to each other safely. Aluminium foil and rock wool were used to prevent heat loss from the setup. Ethylene

glycol whose temperature was adjusted at 0 ºC was circulated in expermental setup during the experiments. Paratherm brand PID Temperature controller was used to adjust and follow the furnace temperature. Temperature in reactor were followed with Elimko 2000 brand digital indicator. After the experiments, whole glass equipment except from reactor was weighed again to compute bio-oil yield. Because the reactor was full with only solid residue after the runs. Gaseous products was not collected. Semi batch experimental setup was shown in Fig 3.

The runs were started with thermal pyrolysis of SP which was carried out at 570 and 520 ºC. Then effect of PS and LDPE adding to the SP was investigated. In our previous study, we have obtained maximum liquid yield for LDPE at 520 ºC, for PS at 570 ºC (Özçakır & Karaduman, 2020a). Because of this, co-pyrolytic experiments were carried out for SP/PS at 570 ºC and for SP/LDPE at 520 ºC. Individually PS and LDPE were added to the feed at the ratios of 33, 50 and 67%. Then, the SP/PS and SP/LDPE feeds which gave the maximum bio-oil yields were tested to the existence of 0.5, 1 and 1.5 grams H-ZSM-5. Lastly, the SP/PS and SP/LDPE feeds with suitable dosage of H-ZSM-5 which was obtained the maximum bio-oil yields were tested with Ni and Co loaded catalysts at the same dosage.



1 Nitrogen bottle **2** Regulator **3** Needle valve **4** Flow meter **5** PID Temperature Controller
6 Thermocouple for furnace **7** Thermocouple for reactor **8** Furnace and reactor system **9** Condenser
10 Phase separator

Figure 3. Pyrolysis setup (Çelikgöğüs & Karaduman, 2015).

2.4 GC-MS Analysis

The bio-oil products were analyzed by utilizing Thermo Finnigan brand DSQ 250 model GC-MS equipment. Capillary column which was inside the instrument was Zebron Brand. The column had 0.25 mm inner diameter and 60 m length. Temperature of the column was arranged prior to automatic injection of the sample. To begin with, the sample was held at 45 ºC for 4 min. Then, temperature was increased to 280 ºC with 3ºC/min heating rate. After that, temperature was preserved at that temperature for 20 min. Total analyzing time was specified as nearly 100 min.

2.5 Determination of coke amount

Firstly the procedure which was included drying in furnace at 200ºC during 2 hours and holding at 25 ºC during 0.5 hours was applied to the used catalysts in the co-pyrolysis experiments. After the catalysts had constant weight value which was symbolized to m_1, the procedure was finished. Then, temperature programme which was shown in Fig 4 was fixed to the furnace and coke removing was started. After then, the same procedure was applied till the weight of the catalysts did not change. That weight was symbolized as m_2. Coke amount on the catalysts was computed by taking the difference between m_1 and m_2.

3. Results and Discussion

3.1 Catalytic co-pyrolysis of SP and PS

Effect of PS adding in feed on bio-oil amount was shown in Fig 5. Considering the results, it was concluded that PS adding caused to the increase in bio-oil yield on a regular basis. It was an expected result. Shadangi & Mohanty have also found that polystyrene adding to the feed increased bio-oil yield from approximately 30 to 60 wt./wt. % at 550 ºC (Shadangi & Mohanty, 2015). Maximum yield for SP and PS co-pyrolysis was obtained as 67.2% at

570 ºC and the ratio of 1/2 SP/PS. Chemical composition of this bio-oil was given in Tab 1. It was found that PS and SP pyrolytic bio-oil comprised of nitrogenous compunds like pyrrole, indole and amide, oxygenated compounds like m-cresol, palmitic acid, nonadecanol and aromatic hydrocarbons which had high peak area percentage. Area percentage of Benzene-Toluene-Ethyl benzene-Xylene (BTEX) fraction and Styrene derivatives were obtained as 11.4 and 76.41 respectively in the bio-oil. In our study in 2020, area percentage of BTEX fraction of microalgae have been found as nearly 2 at 520 ºC (Özçakır & Karaduman, 2020b). Regarding this result, it can be concluded that PS adding to the feed rose BTEX fraction yield.

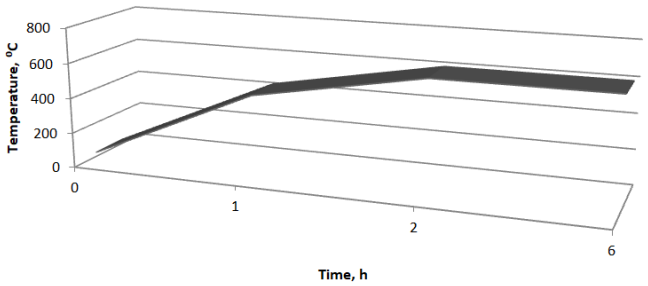


Figure 4. Coke removing steps.

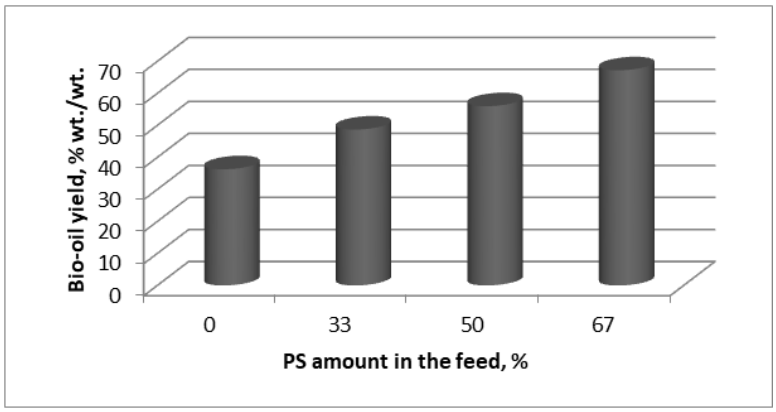


Figure 5. Change in bio-oil amount for SP and PS at 570 ºC.

Table 1. Components in bio-oil of SP1PS2 that was obtained at 570 ºC.

Retention time, min	Component	Formula	Peak area, %
6.83	benzene	C_6H_6	0.16
9.26	pyrrole	C_4H_5N	0.13
10.19	toluene	C_7H_8	7.16
14.38	Ethylbenzene	C_8H_{10}	4.05
14.83	o-xylene	C_8H_{10}	0.03
16.43	styrene	C_8H_8	63.88
17.66	cumene	C_9H_{12}	0.31
20.63	Alpha-methylstyrene	C_9H_{10}	6.44
22.68	Benzene, 2-propenyl-	C_9H_{10}	0.2
24.91	m-cresol	C_7H_8O	0.1
30.36	naphthalene	$C_{10}H_8$	0.05
36.43	Palmitic acid	$C_{16}H_{32}O_2$	0.07
36.93	octadecane	$C_{18}H_{38}$	0.03
39.04	3-methyl-1H-indole	C_9H_9N	0.03
40.85	nonadecanol	$C_{19}H_{40}O$	0.06
45.26	bibenzyl	$C_{14}H_{14}$	0.5
53.32	Styrene dimer	$C_{16}H_{18}$	6.09
67.28	hexadecanamide	$C_{16}H_{33}NO$	0.04

Catalytic experiments were carried out with the feed which had the ratio of 1/2 SP/PS at 570 ºC. Firstly, effect of H-ZSM-5/Feed ratio on bio-oil yield was tested. After then, the metals (Ni/Co) was loaded on H-ZSM-5 and their effectiveness on bio-oil yield was tested by using that ratio. As shown in Fig 6, it was deduced that up to 1 g of the catalyst did not affect the bio-oil yield and above 1 g catalyst, bio-oil yield decreased. This was an expected result. Mo et al. have also found that H-ZSM-5 using almost did not change *Spirulina*'s bio-oil yield under Nitrogen atmosphere (Mo et al., 2020). Another study have shown that Silica-Alumina catalyst decreased bio-oil yield of *Spirulina* up to 10% at 550 ºC (Jamilatun et al., 2020). The maximum yield was obtained as 63.5% for 1/15 H-ZSM-5/Feed ratio. As shown in Fig 7, Ni or Co loading on catalyst decreased the bio-oil yield under that yield. But, nearly same amount of bio-oil was obtaining both Ni (56.3%) and Co (55%).

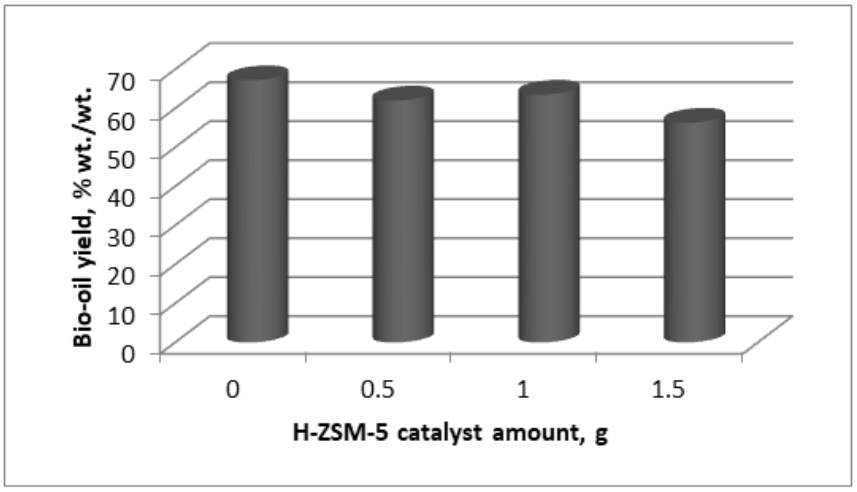


Figure 6. Effect of H-ZSM-5 on bio-oil yield for SP and PS co-pyrolysis at 570 ºC.

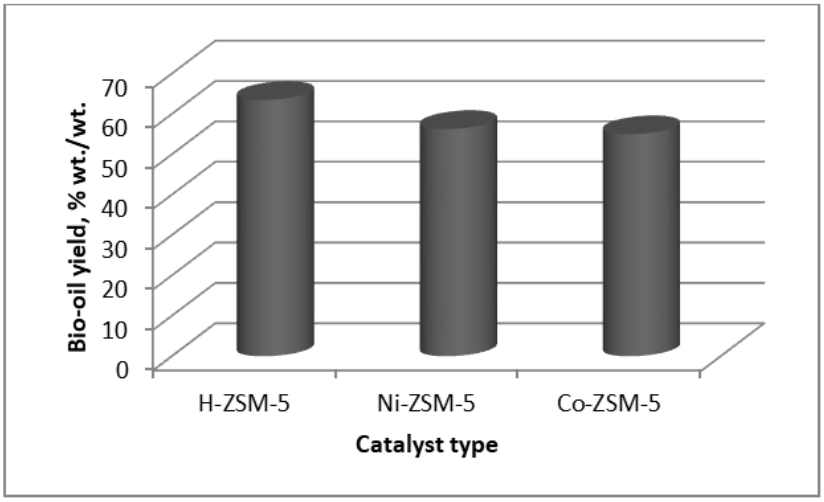


Figure 7. Effect of metal loading on H-ZSM-5 on bio-oil yield for SP and PS co-pyrolysis at 570 ºC.

Benzene, o-xylene and naphthalene peak areas in the bio-oils were converted to mass values by multiplying theirs MS detector mass response factors which was given in Tab 2. Then, mass values of the components were summed. And then, mass percentage value of each component was obtained in the bio-oil. It was assumped that bio-oils comprised of only that components, because the response factors of other components in bio-oil were not found in the literature.

Table 2. Detector response factors for some aromatic compounds in bio oil (URL-1, 2015).

Aromatic compound	MS detector mass response
Benzene	1.135
o-xylene	1.138
naphthalene	1.860

As shown in Fig 8, H-ZSM-5 catalyst using led to increase of naphthalene amount in bio-oil. In addition, naphthalene amount increased with increasing catalyst amount. The amount of o-xylene did not affect from catalyst using. Benzene amount tended to increase when catalyst amount increased from 1 to 1.5 g. As shown in Fig 9, metal loading on catalyst did not affect the amount of selected aromatic component in the bio-oil significantly. Che et al. have examined the effect of Zn, Fe, Ca, Ce and La loaded ZSM-5 on benzene and xylene yield during biomass pyrolysis. They concluded the result that excessive metal loading (10%) can cause to decrease diffusion ability and acidity of ZSM-5 (Che et al, 2019). It was thought that same situation can also happen our study for Ni and Co metals so benzene and o-xylene yield did not change. When it was used 1 g Ni-ZSM-5, it was obtained minimum amount of o-xylene (0.06%) and benzene (0.30%). For naphthalene, minimum amount was obtained by using Co-ZSM-5 (0.47%).

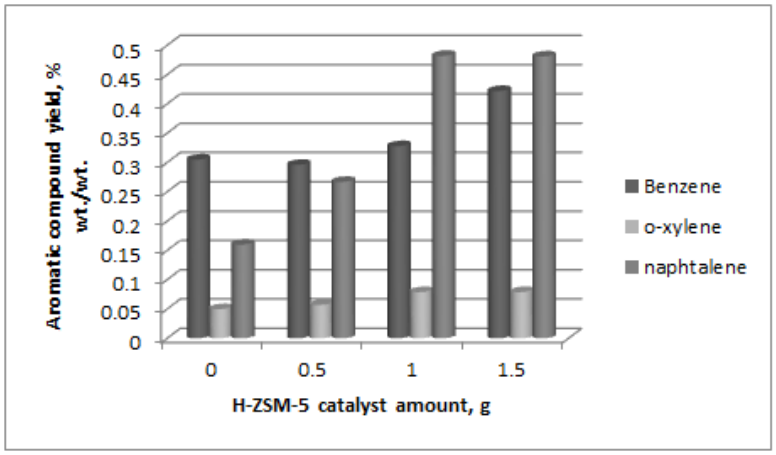


Figure 8. Effect of H-ZSM-5 on some aromatic compounds yield for SP and PS co-pyrolysis at 570 ºC.

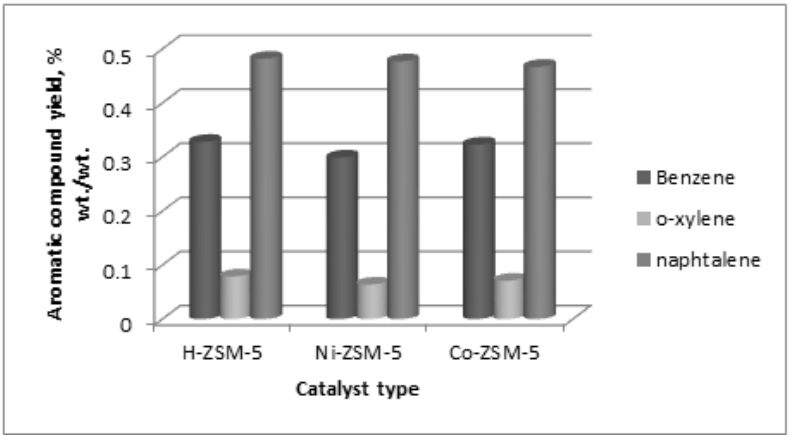


Figure 9. Effect of metal loading on H-ZSM-5 on some aromatic compounds yield for SP and PS co-pyrolysis at 570 ºC.

Coke percentage was obtained as 13.602 in case of HZSM-5 catalyst using for SP and PS co-pyrolysis. Ni-ZSM-5 affected on coke minimization (10.784 %). Co-ZSM-5 did not change coke percentage importantly (13.251 %). Javaid et al (2015) have reached that benzene and xylene caused to coke on H-ZSM-5 in their study (Javaid et al.,

2015). As mentioned before, the minimum xylene and benzene amount was obtained when Ni-ZSM-5 was used. It can be thought that Ni help degradation of benzene and xylene on the catalyst surface during the co-pyrolysis.

3.2 Catalytic co-pyrolysis of SP and LDPE

Effect of LDPE adding in feed on bio-oil amount was shown in Fig 10. Regarding the results, low LDPE adding as 5 g to the feed caused to a little bit decrease in bio-oil yield from 36.3% to 29.1%. Then, it was concluded that LDPE adding which was more 5 g to the feed caused to the increase in bio-oil yield regularly. Maximum yield for SP and LDPE co-pyrolysis was obtained as 54.1% at 520 ºC and the ratio of 1/2 SP/LDPE. Chemical composition of that bio-oil was given in Tab 4. It was found that LDPE and SP pyrolytic bio-oil comprised of nitrogenous compunds like pyrrole, oxygenated compounds like palmitic amide and straight chain/cyclic alkanes and alkenes which had high peak area percentage. The amount of total aromatic hydrocarbon fraction which included benzene, ethylbenzene, styrene, cumene and naphthalene was found as 1.28%.

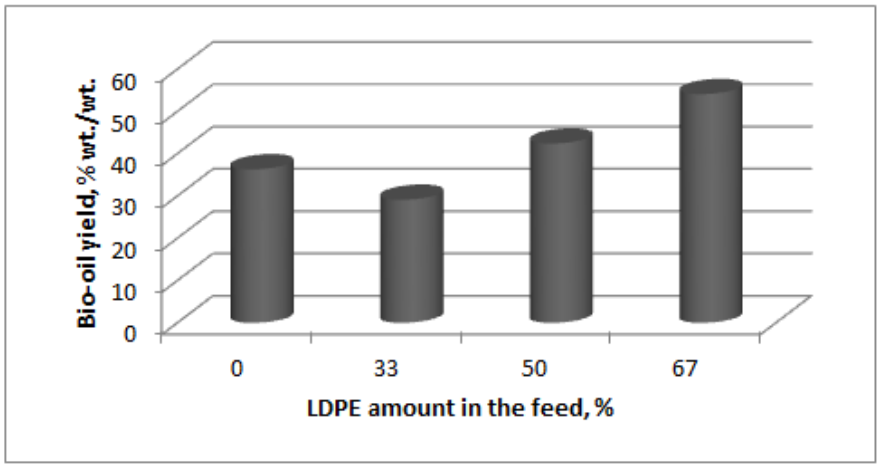


Figure 10. Change in bio-oil amount for SP and LDPE at 520 ºC.

Catalytic experiments were done with the feed which had the ratio of 1/2 SP/LDPE at 520 ºC. The route for SP/LDPE was applied on the same way with SP/PS. As shown in Fig 11, it was deduced that 0.5 g of the catalyst affected the bio-oil yield significantly. Minimum bio–oil yield was taken as 43% at that catalyst amount. For other ratios, it was said that catalyst amount did not affect the bio-oil yield importantly. The maximum yield was obtained as 51.2% for 1/10 H-ZSM-5/Feed ratio. As shown in Fig 12, Ni or Co loading on catalyst reduced the bio-oil yield under that yield. But, nearly same amount of bio-oil was obtaining both Ni (50.4%) and Co (48.9%). Iliopoulou et al. have samely declared that bio-oil yield decreased when Ni and Co metals doped to ZSM-5. As a reason of this situation, they have put forward that yield of gaseous product especially hydrogen and saturated hydrocarbon increased (Iliopoulou et al., 2012).

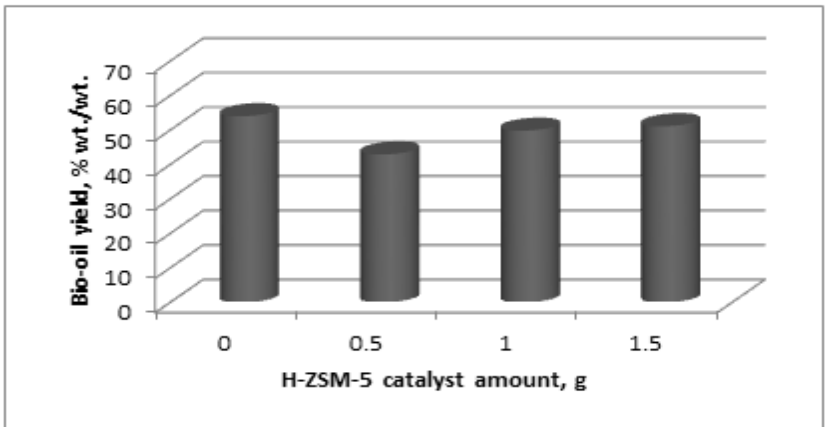


Figure 11. Effect of H-ZSM-5 on bio-oil yield for SP and LDPE co-pyrolysis at 520 ºC.

Benzene, o-xylene and naphthalene peak areas in the bio-oils were converted to mass values on the same way with SP/PS. As given in Fig 13, H-ZSM-5 catalyst using led to increase of benzene amount in bio-oil significantly. The amount of o-xylene did not affect from catalyst using. In addition, o-xylene amount increased with increasing catalyst amount slightly. Naphthalene amount tended to increase when catalyst amount increased from 0.5 to 1.5 g. As shown in Fig 14, metal loading on catalyst did not affect the amount of selected aromatic component in the bio-oil significantly. Yao et al. have also declared that benzene, o-xylene and naphtalene yield did not change importantly with Ni loading for LDPE and biomass co-pyrolysis (Yao et al, 2015). Veses et al. have clarified the reason of this situation. They have claimed that metal incorporation can come right on top of ion states of the cation form zeolite. Because of this reason, acid sites of the zeolite can decreased and aromatic yield nearly did not change (Veses et al., 2016). When it was used 1.5 g H-ZSM-5, it was obtained minimum amount of o-xylene (15.836%) and benzene (17.915%). For naphthalene, minimum amount was obtained by using Co-ZSM-5 (8.484%). It was obtained nearly the same amount by using Ni-ZSM-5 (8.59%).

Table 4. Components in bio-oil of SP1LDPE2 that was obtained at 520 ºC.

Retention time, min	Component	Formula	Peak area, %
4.6	Cyclobutane, methyl-	C_5H_{10}	0.61
5.18	Cyclopentene	C_5H_8	0.11
5.62	1-hexene	C_6H_{12}	1.82
6.77	benzene	C_6H_6	0.21
7.43	cyclohexene	C_6H_{10}	0.19
7.81	1-heptene	C_7H_{14}	2.34
8.15	Hexane, 3-methyl-	C_7H_{16}	1.48
8.83	Cyclohexane, methyl-	C_7H_{14}	0.27
9.22	pyrrole	C_4H_5N	0.41
10.51	Cyclohexene, 4-methyl-	C_7H_{12}	0.38
14.29	ethylbenzene	C_8H_{10}	0.12
14.55	o-xylene	C_8H_{10}	0.2
15.75	styrene	C_8H_8	0.64
17.02	nonane	C_9H_{20}	1.53
17.53	cumene	C_9H_{12}	0.15
19.17	Cyclopentene, 1-butyl-	C_9H_{16}	0.17
20.66	1-hexene, 2-methyl-	C_7H_{14}	0.27
21.34	1-decene	$C_{10}H_{20}$	0.26
22.3	decane	$C_{10}H_{22}$	1.36
23.13	cyclodecene	$C_{10}H_{18}$	0.21
27.49	undecane	$C_{11}H_{24}$	1.61
30.37	naphthalene	$C_{10}H_8$	0.08
34.46	cyclododecene	$C_{12}H_{22}$	0.22
36.6	1-pentadecene	$C_{15}H_{30}$	2.86
37.09	pentadecane	$C_{15}H_{32}$	1.52
41.49	nonadecane	$C_{19}H_{40}$	1.55
41.9	1-nonadecene	$C_{19}H_{38}$	0.2
45.23	1-octadecene	$C_{18}H_{36}$	2.97
45.64	octadecane	$C_{18}H_{38}$	1.78
46.03	cyclopentadecane	$C_{15}H_{30}$	0.15
49.17	1-docosene	$C_{22}H_{44}$	2.67
49.95	1-eicosene	$C_{20}H_{40}$	0.17
52.92	heptadecene	$C_{17}H_{34}$	2.55
53.28	eicosane	$C_{20}H_{42}$	1.88
56.47	hexadecene	$C_{16}H_{32}$	2.49
56.79	hexadecane	$C_{16}H_{34}$	1.55
60.15	heneicosane	$C_{21}H_{44}$	1.54
63.07	9-nonadecene	$C_{19}H_{38}$	1.99
63.36	eicosane	$C_{20}H_{42}$	1.52
67.33	Palmitic amide	$C_{16}H_{33}NO$	0.15
69.32	Pentacosane	$C_{25}H_{52}$	1.27
74.76	octacosane	$C_{28}H_{58}$	0.74

Coke percentage was obtained as 12.550 in case of HZSM-5 catalyst using for SP and LDPE co-pyrolysis. Both Ni (13.645 %) and Co (17.149 %) increased coke deposition. Relatively, Ni-ZSM-5 had less coke. That situation can be explained on the same way with SP/PS. Besides that, popular wisdom which was metal using prevented coke formation on ZSM-5 for bio-oil production fell into decay with that result.

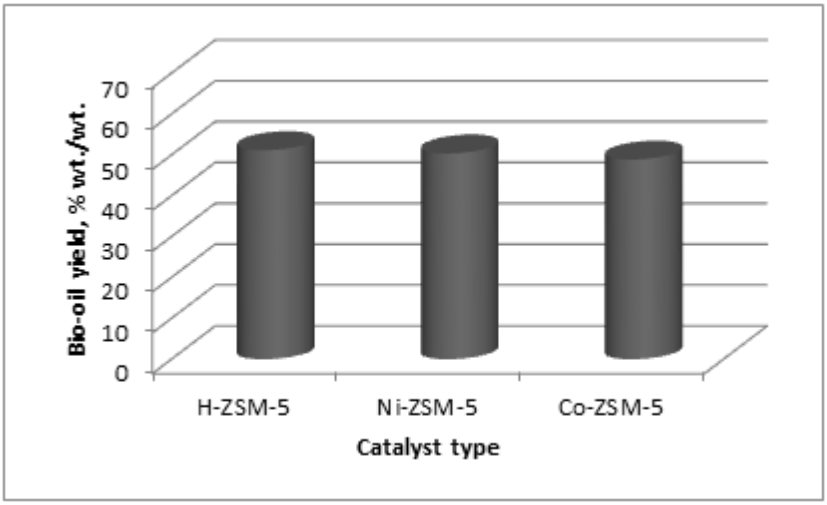


Figure 12. Effect of metal loading on H-ZSM-5 on bio-oil yield for SP and LDPE co-pyrolysis at 520 ºC.

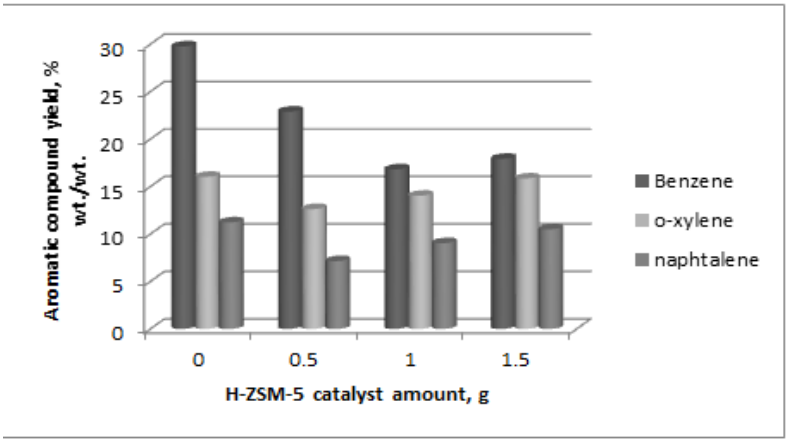


Figure 13. Effect of H-ZSM-5 on some aromatic compounds yield for SP and LDPE co-pyrolysis at 520 ºC.

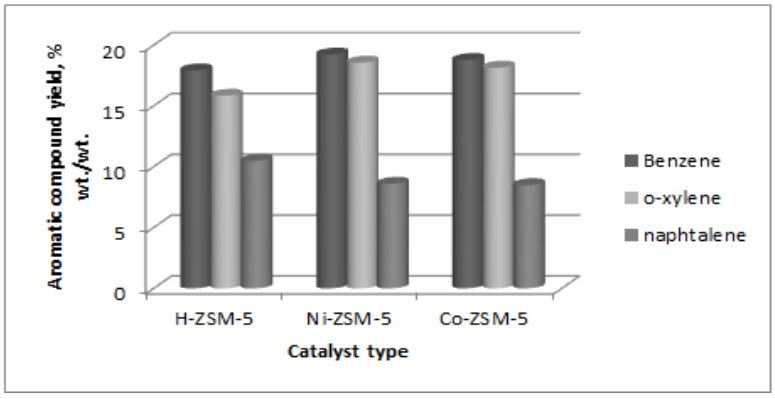


Figure 14. Effect of metal loading on H-ZSM-5 on some aromatic compounds yield for SP and LDPE co-pyrolysis at 520 ºC.

4. Conclusion

For SP and PS co-pyrolysis, maximum bio-oil amount was obtained as 67.2% by weight at 570 ºC and 1/2 ratio of SP to PS. 1 g of H-ZSM-5 catalyst and Ni-ZSM-5 using decreased that amount in the proportion of almost 4% and 11% by weight respectively. At a result of the catalytic co-pyrolysis of SP and PS on H-ZSM-5, it was found that PS and SP pyrolytic bio-oil comprised of nitrogenous compunds like pyrrole, indole and amide, oxygenated compounds like m-cresol, palmitic acid, nonadecanol and aromatic hydrocarbons which had high peak area percentage.Area percentage of Benzene-Toluene-Ethyl benzene-Xylene (BTEX) fraction and Styrene derivatives were obtained as 11.4 and 76.41 respectively in the bio-oil. It was also determined that metal loading on the catalyst did not affect the amount of selected aromatic components which were benzene, toluene and naphthalene in the bio-oil significantly. The coke amount of the catalysts were found as 13.602% for H-ZSM-5, as 10.784% for Ni-ZSM-5 and as 13.251% for Co-ZSM-5. For SP and PS co-pyrolysis, it was obtained that Nickel doping was the effective way in coke minimization.

For SP and LDPE co-pyrolysis, maximum bio-oil amount was taken as 54.1% by weight at 520 ºC and 1/2 ratio of SP to LDPE. 1.5 g of H-ZSM-5 catalyst and Ni-ZSM-5 using decreased that amount in the proportion of almost 3% and 4% by weight respectively. At a result of the catalytic co-pyrolysis of SP and LDPE on H-ZSM-5, it was determined that bio-oil comprised of nitrogenous compunds like pyrrole, oxygenated compounds like palmitic amide and straight chain/cyclic alkanes and alkenes which had high peak area percentage. The amount of total aromatic hydrocarbon fraction which included benzene, ethylbenzene, styrene, cumene and naphthalene was found as 1.28%. It was also determined that metal loading on the catalyst increased benzene and o-xylene amount while it decreased naphthalene amount in the bio-oil. The coke amount of the catalysts were found as 12.550% for H-ZSM-5, as 13.645% for Ni-ZSM-5 and as 17.149% for Co-ZSM-5. For SP and LDPE co-pyrolysis, it was found that Nickel was the most effective metal in coke minimization.

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