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Research Article

Optimization of Synthesis of Ethyl Acetate by Response Surface Method and Investigation of Reactive Sorption Effect of Hydrogel in Synthesis

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Abstract

In this study, ethyl acetate synthesis is made from ethyl alcohol and acetic acid. Ethyl acetate is used as solvent and alternative fuel additive The synthesis was optimized by the surface response method. The effects of temperature, catalyst amount and reactant initial molar ratio on acid conversion in the reaction were investigated. Sulfo succinic acid was used as the catalyst. Conversion values were increased with increase in initial molar ratio, increase in catalyst amount, and increase in temperature. In this study, poly vinyl alcohol hydrogels were also prepared for reactive sorption application. Hydrogels were added to the reactor under certain operating conditions and used in the esterification reaction. It was observed that the conversion increased by using hydrogels together with catalyst. Ethyl acetate synthesis was optimized by using the student version of the Design Expert software. 12th version of the Design Expert program was used. Optimization was made with the center composite design method by using response surface method. Quadratic model is proposed by the program. Experimental data and model data were found compatible with each other. Optimum values for conversion are variables that the temperature is 80 °C, the amount of catalyst is 1% and the initial molar ratio is 5. The highest conversion value of 89.35% could be achieved by the optimum values. The study has also shown that the conversion values can be increased by sorping water by using hydrogels. According to Le Chatelier's principle sorption of water shifts the esterification reaction towards the products also.

Keywords: Optimization, Quadratic model, Ethyl acetate.

Yüzey Yanıt Yöntemi İle Etil Asetat Sentezinin Optimizasyonu Ve Sentezde Hidrojelin Reaktif Sorpsiyon Etkisinin İncelenmesi

Öz

Bu çalışmada etil alkol ve asetik asit kullanarak etil asetat sentezi yapılmıştır. Etil asetat çözücü ve yakıt katkısı olarak kullanılmaktadır. Sentez yüzey yanıt yöntemi ile optimize edilmiştir. Sıcaklık, katalizör miktarı ve reaktan başlangıç molar oranının asit dönüşümü üzerindeki etkileri incelenmiştir. Sulfo süksinik asit katalizör olarak kullanılmıştır. Dönüşüm değerleri başlangıç molar oranındaki artış, katalizör miktarındaki artış ve sıcaklıktaki artış ile artmıştır. Bu çalışmada polivinil alkol hidrojeller de reaktif sorpsiyon uygulaması için hazırlanmıştır. Hidrojeller belli çalışma koşullarında rektöre eklenmiş ve esterleşme reaksiyonunda kullanılmıştır. Katalizör ile birlikte hidrojel kullanımının dönüşümü arttırdığı görülmüştür. Etil asetat sentezi Design Expert program ile optimize edilmiştir. Programın 12. versiyonu kullanılmıştır. Optimizasyon Yüzey Yanıt Yöntemi Merkezi Kompozit Tasarım Metodu ile yapılmıştır. Program tarfından Quadratik model önerilmiştir. Deneysel veriler ile model verilerinin birbirleriyle uyumlu olduğu görülmüştür. Dönüşüm için optimum değişkenler 80°C sıcaklık, % 1 katalizör miktarı, 5 başlangıç molar oranıdır. Optimum değerlerde elde edilecek en yüksek dönüşüm % 89.35 dir. Çalışma ayrıca hidrojel kullanılarak su tutulmasıyla dönüşümün arttırılabileceğini göstermiştir. Le Chatelier's prensibine göre suyun sorplanması esterleşme reaksiyonunu ürünler yönüne kaydırmıştır.

Anahtar Kelimeler: Optimizasyon, Quadratik model, Etil asetat.

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1. Introduction

When ethanol is blended with gasoline fuel, volatility and phase stability problems occur. Phase separation makes fuel quality bad and corrosion in the engine (Ezis at all, 2018a). Ethanol is an additive for gasoline. Its advantages are increasing of octane number, decreasing of toxic emissions and lower cost. But ethanol absorps water from environment such as moisture in the storage tanks. This causes phase separation. Adding ethyl acetate to hydrous ethanol increases phase stability and octane number (Ezis at all, 2018b).

Esters are used as solvents, thinners and flavorings in the chemical industry, pharmaceuticals, cosmetics and paint industries generally. An ester is formed as a result of the reaction of carboxylic acid and alcohol by using a catalyst. Water is also formed as a by-product in the reaction. Esterification reactions are equilibrium reactions. In order to progress the reaction to towards the product, it is necessary to use excess reactant or to separate the by-product. The use of excess reactant is not economical. The excess reactant increases the ester as well as the water and requires an extra cost for the product separation. It is a more economical to capture the by-product water in the reaction medium. The retain of water would also ease the purification of the ester which is product (Wang at all, 2018; Soltani at all, 2017; Sirsam at all, 2016).

Ethyl acetate is widely used in industry because of a good solvent. Ethyl acetate is selected in many sectors due to its low production cost, non-toxicity and nice smell. Ethyl acetate is synthesized from ethyl alcohol and acetic acid by the esterification reaction. The reaction can be carrieed out by an acidic catalyst. The variables that affect acid conversion in esterification reactions are temperature, amount of catalyst, and initial molar ratio of reactant (Hasırcı at all, 2018). Sulfo succinic acid is a successful catalyst among acidic catalysts (Hasırcı at all, 2019).

In this study, sulfo succinic acid was used as the catalyst. The reaction was taken place in the batch reactor under reflux. The effects of temperature, amount of catalyst, initial molar ratio of reactant on conversion were investigated. The reaction time is taken as 3 hours. Acid conversion in the esterification reaction was determined by titration method (Yenihan Yüzer at all, 2019a, Yenihan Yüzer, N. 2019b).

In this study, hydrogels were also prepared using poly vinyl alcohol polymer. The prepared hydrogels were added to the reactor under operating conditions that were decided and used in the esterification reaction to see reactive effect.

Hydrogels are hydrophilic polymeric structures that can sorp water and retain very high water inside. The solubility of the polymer in liquid phase is prevented by cross-linking. The cross-linked polymer swells as a result of water sorption without dissolving. (Aurand at all, 2013). Polyvinyl alcohol is a hydrophilic polymer that has good mechanical strength.. (Fu X. at all, 2017; Mok at all, 2020).

The aim of the study is to examine the effects of the factors that are temperature, catalyst amount, reactant initial molar ratio in ethyl acetate synthesis on the conversion values by the response surface method and to find the optimum reaction conditions.

Response surface method (RSM) is a statistical method. The modelling is done by analyzing the response of any process to independent variables called factors. The responses to the variables are estimated by the model equation obtained by RSM. The responses are predicted without making experiment also. Thus, time and cost are decreased by optimization (Yüksel, 2018). The relationship between independent variables is determined for getting optimum process conditions by RSM (Turki at all, 2021). Optimizations with RSM using Design Expert program are applied in the different specific areas (Mortas at all, 2020, Bekdeşer 2019, Çolak at all, 2018). There are two types of RSM, known as Central Composite Design (CDD) and Box Behnken Design (BBD). RSM uses least square method for fitting model to experimental data (Manojkumar at all, 2020).

RSM determines accuracy of experimental data. The responses to factors are estimated with accuracy at the limits of the determined variables (Hilmioğlu at all, 2021).

In this study, the effects of factors on the response were investigated using the central composite design (CCD) method. The variables that are temperature, catalyst amount, reactant initial molar ratio were selected as factors. The response is also the conversion value obtained at the end of the reaction.

2. Material and Method

2.1. Material

PVA polymer; (Mw~125.000), acetic acid, ethyl alcohol, sulfo succinic acid, gluteraldehit (%50 wt. in H_2O) were taken from Sigma-Aldrich.

2.2. Method

2.2.1. Preparation of PVA Hydrogel

The polymeric solution was prepared using poly(vinyl alcohol) polymer solid and water. 5% PVA solution was prepared at a constant temperature of 90°C under reflux. The polymer solution was cross-linked with glutaraldehyde. Hydrogel beads were formed by dripping the PVA solution into the mixture consist of methanol and NaOH. pH was adjusted by washing with water then, the hydrogels were filtered and dried.

2.2.2. Synthesis Reaction

For the application of RSM in ethyl acetate synthesis, ethyl alcohol/ acetic acid initial molar ratios were 1:1, 3:1, 5:1; temperature were 60, 70, 80 °C, the amounts of sulfosuccinic acid catalyst (by weight, based on acid) were 0.1-0.55-1 %. The reaction was carried out in the batch reactor under reflux during 3 hours.

In order to see the hydrogel's reactive effect, the process variables were selected as follows .The catalyst amount was 1%, the initial molar ratio was 6:1, the temperature was 75°C, and the experiments were done for 3 hours by adding 0.1 g, 0.3 g, 0.5 g hydrogel to the reactor.

2.2.3. Sorption Test

The water sorption capacity of the prepared hydrogels was determined by sorption tests. Firstly hydrogel was weighted for determining dry weight. The hydrogel was put in water for a time then dried gently and weighed to determine wet weight. The swelling degree was calculated using the dry hydrogel weight and the wet hydrogel weight. Degree of swelling (DS) was etimated by Equation 1.

$$DS\ (\%) = \frac{wet\ weight - dry\ weight}{dry\ weight} \times 100 \qquad (1)$$

2.2.4. Titration method

The acid is titrated by using basic KOH solution and the acid conversion is calculated. Initially, (t=0) small amount of reaction mixture (0.1 ml) is titrated by KOH solution (0.1 M) with using phenolphthalein indicator. Thus ,the initial acid concentration value is found by titration. Titration is repeated for every hour by taking samples from the reaction mixture.

The conversion values are calculated by Equation 2 (Yenihan Yüzer, N. 2019 b)

$$\text{Conversion (\%)} = \frac{\text{initial moles of acid} - \text{moles of acid at anytime}}{\text{initial moles of acid}} \times 100 \qquad (2)$$

3. Results and Discussion

3.1. Reaction and Sorption Results

In order to examine the effect of variables on conversion reactant (ethyl alcohol/ acetic acid) initial molar ratio were selected as 1:1, 3.5:1, 5:1; temperature was selected as 75 °C; the amount of catalyst sulfosuccinic acid (by weight of acid) was selected as 0.1%. The reaction was carried out in a batch reactor for 3 hours. The results obtained were given in Figure 1.

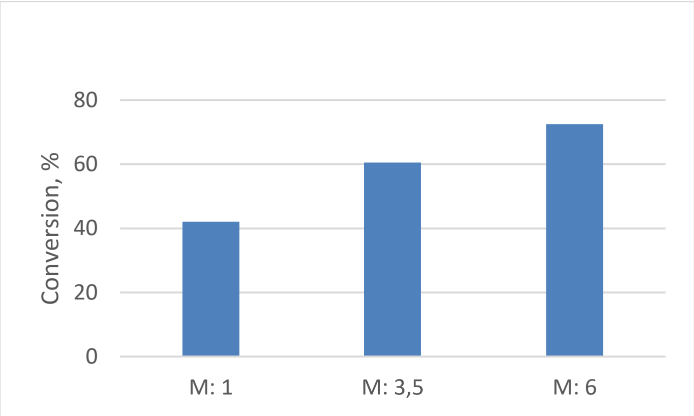

Figure 1 Molar ratio effect on conversion (Time: 3 h, Catalyst: %0,1, T: 75°C) (Molar oranın dönüşüm üzerindeki etkisi)

To examine the effect of the catalyst amount on the conversion, the reaction was carried out for 3 hours in the batch reactor with catalyst amounts of 0.1%, 0.55%, 1%, reactant initial molar ratio of 6 and temperature of 75°C. Obtained results were given in Figure 2.

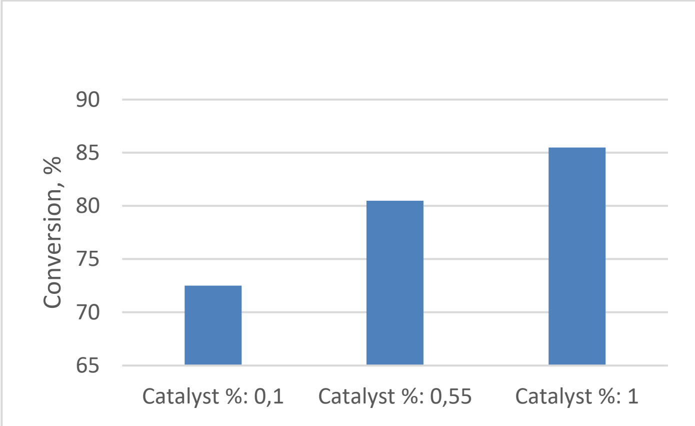

Figure 2 Catalyst amount effect on conversion (Time: 3 h, M: 6, T: 75°C) (Katalizör miktarının dönüşüm üzerindeki etkisi)

It was observed that the increase in the reactant initial molar ratio and the amount of catalyst increased the conversion also.

In order to see the contribution of hydrogel spheres in the ethyl acetate synthesis reaction, 0.1 g, 0.3 g, 0.5 g hydrogel were added and the reaction was carried out for 3 hours in the batch reactor with a catalyst amount of 1%, a reactant initial molar ratio of 6 and a temperature of 75°C. Results obtained were given in Figure 3.

When the amount of hydrogel was higher, the conversion increased.

In order to compare the conversion obtained by using only catalyst and the conversion obtained by using catalyst together with hydrogel, 0.5 g hydrogel was added to the reactor and the reaction was carried out for 3 hours where the catalyst amount was 1%, the initial molar ratio was 6, and the temperature was 75°C. The results were given in Figure 4.

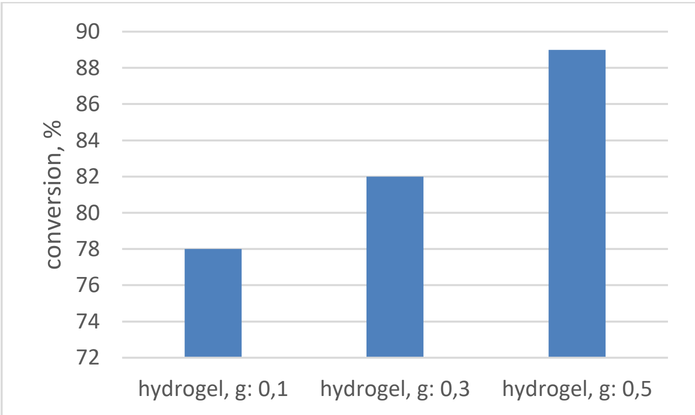

Figure 3 Hydrogel amount effect on conversion (Time: 3 h, M: 6, Catalyst: % 1, T: 75°C) (Hidrojel miktarının dönüşüm üzerindeki etkisi)

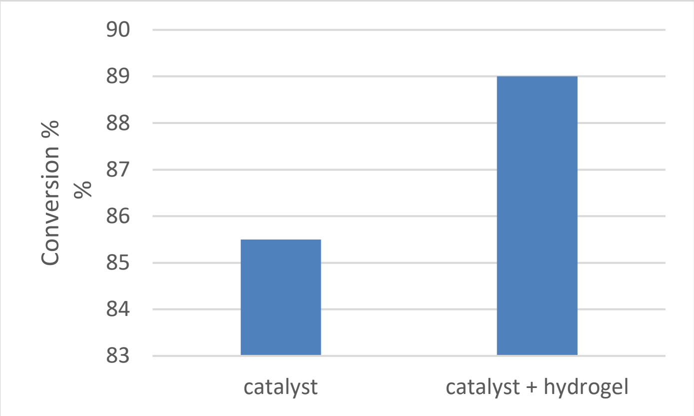

Figure 4 Catalyst together with hydrogel effect on conversion (Time: 3 h, M: 6, Catalyst: %1, Hydrogel: 0,5 g, T: 75°C) (Katalizör ve hidrojelin dönüşümün üzerindeki etkisi)

It was observed that the hydrogel additive had a positive effect on the conversion value.

The water retaining capacities of the hydrogels used were determined by sorption tests and were given in Figure 5.

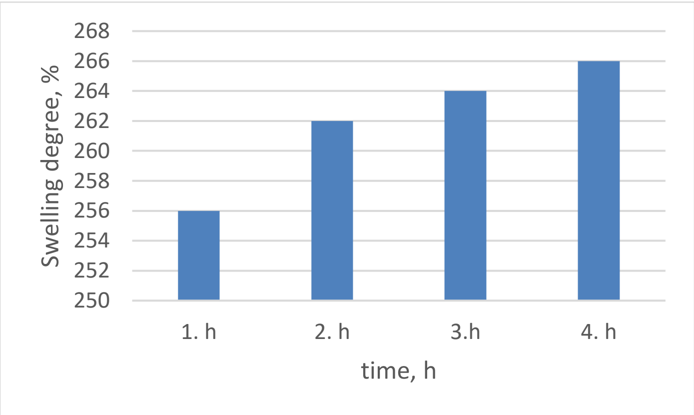

Figure 5 Sorption values of water by hydrogel (Hidrojelin su sorplama değerleri)

It has been calculated that the PVA hydrogel globules prepared can absorb water at a rate of 266%. This value showed that the prepared PVA hydrogels could be used in the esterification reactions due to their high hydrophilicity (Hilmioğlu at all, 2020).

The reason of the increase in the conversion by means of the hydrogel is that the hydrogel retains the by-product water and shifts the reaction towards the products. The swelling degree values expressing the water holding capacity of the hydrogels determined by the sorption tests are quite high .

It is concluded that due to the hydrophilicity, hydrogel spheres keeps the by-product water in the structure and this situation allows the reaction to shift forward direction according to the Le Chatelier principle.

3.2. Statistical Modelling Results

3.2.1. Factors and Responses

60°C, 70°C, 80°C as temperature values; 0.1%, 0.55%, 1% as catalyst amount values; 1, 3, 5 as reactant initial molar ratio values were selected, ethyl acetate synthesis was performed for these variables and acetic acid conversion was calculated.

A (temperature), B (catalyst amount), C (initial molar ratio) were selected as variables. The conversion value was response to A, B, C factors. The program that uses CCD method suggested 19 experiments for factor values selected.

3.2.2. Fit Summary

Fit summary data for all models were given in Table 1 and for the Quadratic model suggested in Table 2.

In Table 1, the low standard deviation, high R^2 values and low press value were examined, it was seen that the data were analyzed by the best Quadratic model in the program.

In Table 2, the difference between the predicted regression coefficient R2 (0.8980) and the adjusted regression coefficient R2 (0.9652) is less than 0.2. This indicates the suitability of the model. The fact that the regression coefficient R2 value is close to 1 also indicates that the model is fit. For the model to be meaningful, a adequate precision value that represents the signal to noise ratio must be greater than 4. Because the model used has adequate precision 33.2001, it can be said that the model is compatible with the data.

3.2.3. Response Equation

The Quadratic model equation of RSM and CCD for the conversion value (%) was found as shown below. Conversion values as responses were estimated by the program at the values determined of the A (temperature), B (catalyst amount), C (initial molar ratio) as factors.

$$\text{Conversion (\%)} = 67{,}23 + 8{,}03*A + 9*B + 9{,}77*C - 0{,}0250*AB + 0{,}5*AC - 2{,}45*BC - 1{,}08*A^2 + 2{,}07*B^2 - 3{,}68*C^2$$

According to this equation, the conversion primarily depends on the variables A (temperature), B (catalyst amount, C (initial molar ratio). The most influential factor in the response is C factor.

The response equation is an equation that calculates the conversion value for variables called factors. It calculates conversion values as response for any untested variable values such as different temparatures, different initial reactant molar ratios, different catalyst amounts as factors.

3.2.4. Anova Analysis

ANOVA analysis was given in Table 3 for the quadratic model of central composite method.

The F value of the Quadratic model is 56.48, that shows the importance of this model. The higher the F value, the higher the accuracy of the model.

It is known that terms with a p value less than 0.0500 are important. In this case, it can be said that A, B, C, BC, C^2 are important model terms.

A $p< 0.05$ indicates that the model predictions are in the 95% confidence interval according to the statistical significance level of the model.

The fact that the p value is less than 0.05, the adeqate precision value is greater than 4, and the difference between the adjusted regression coefficient and the predicted regression coefficient is less than 0.2 indicate the suitability of the Quadratic model.

The value that has highest F value in the ANOVA table belongs to the variable with the greatest effect on the response. The F-value, p-value, and SS-value indicate the importance of the model. As the SS increases, the importance of that variable also increases. Table 3 is showed that, it is seen that the most important factor in the response is the reactant initial molar ratio of factor C.

Tablo 1 Fit summaries of models (Modeller İçin Uygunluk Verileri)

Source	Standart deviation	R^2	Sequential p value	R^2 Adjusted	R^2 Predicted	Press value	
Linear	3.19	0.9405	<0.0001	0.9285	0.8976	262.36	
2FI	2.92	0.9600	0.1752	0.9400	0.8992	258.23	
Quadratic	2.23	0.9826	0.0488	0.9652	0.8980	261.33	suggested
Cubic	2.22	0.9904	0.4801	0.9654			

Tablo 2 Fit Summary of Quadratic Model (Quadratic Model İçin Uygunluk Verileri)

Standart deviation	2.23	R^2	0.9826
Mean	65.81	Adjusted R^2	0.9652
C.V. %	3.38	Predicted R^2	0.8980
		Adequate precision	33.2001

Tablo 3 ANOVA Analysis of Variance (ANOVA Varyans Analizi)

Source	Sum of Squares, SS	Degree of medium, df	Mean square	F value	P value	
Model	2517.32	9	279.70	56.48	<0.0001	important
A	644.81	1	644.81	130.20	<0.0001	
B	810.00	1	810.00	163.56	<0.0001	
C	954.53	1	954.53	192.75	<0.0001	
AB	0.0050	1	0.0050	0.0010	0.9753	
AC	2.00	1	2.00	0.4039	0.5409	
BC	48.02	1	48.02	9.70	0.0124	
A^2	3.20	1	3.20	0.6471	0.4419	
B^2	11.67	1	11.67	2.36	0.1591	
C^2	37.06	1	37.06	7.48	0.0230	
Residual	44.57	9	4.95			
Lack of fit	44.57	5	8.91			
Pure error	0.0000	4	0.0000			
Cor total	2561.89	18				

3.2.5. Diagnostic Graphics

The graphs in the Fgure 6-9 are diagnostics graphs.

The experimental data were compared with the data estimated by the model in Figure 6.

As seen in Figure 6, the values estimated by the Quadratic model are very close to the experimental real values. This situation shows that the model equation is compatible and can be used safely.

The comparison of the model estimated conversion values with the residual values is shown in Figure 7.

In the chart in Figure 7, it is desired that the data be within the red lines. Only one data (data of experiment 15) is outside the red lines. This experiment can be repeated. The distribution of other data is very appropriate.

Comparison of the residaul values with the number of experiments is given in Figure 8.

Examination of Figure 8 shows that the data has a normal distribution in the form of a zig zag within the red borders. This is a normal situation. Since the data that belongs to the experiment 15 deviates from the distribution, this deviation can be eliminated by repeating this experiment.

The comparison of the number of run with the Cook's distance is given in Figure 9.

When the Cook's distance graph in Figure 9 is examined, it is seen that all data are below the value of 1,this indicates that the data have the expected Cook's distance distribution.

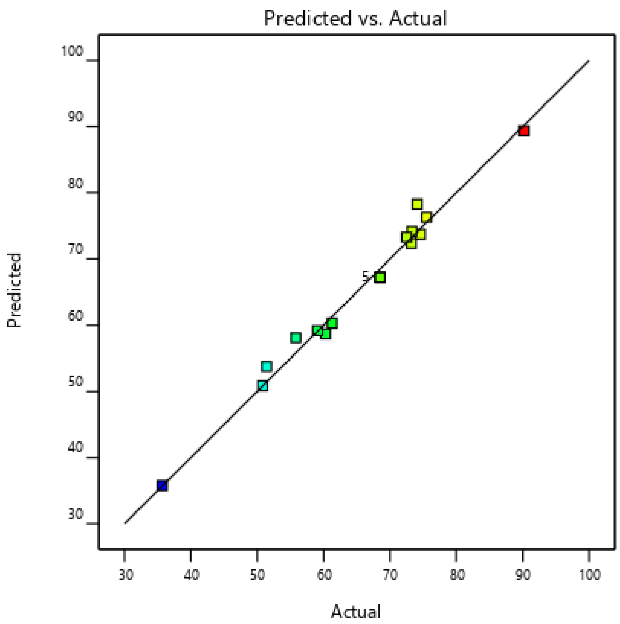

Figure 6 Predicted Conversion Values versus Actual Conversion Values (Model Tahmini Dönüşüm Değerleri ile Gerçek Dönüşüm Değerleri Karşılaştırılması)

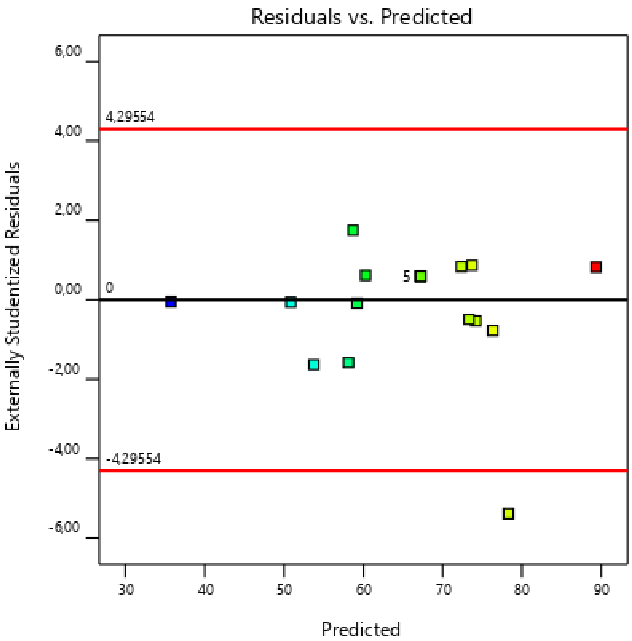

Figure 7 Predicted Conversion Values versus Residuals (Model Tahmini Dönüşüm Değerleri ile Fark Değerleri Karşılaştırılması)

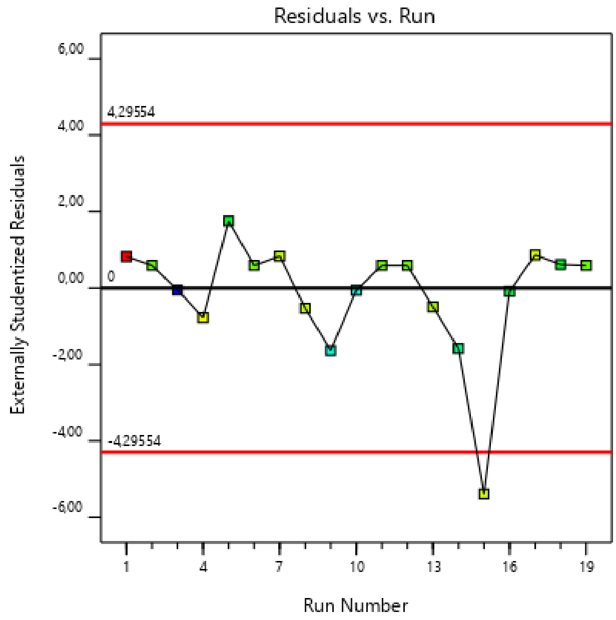

Figure 8 Run Number versus Residuals (Deney Sayısı ile Fark Değerleri Karşılaştırılması)

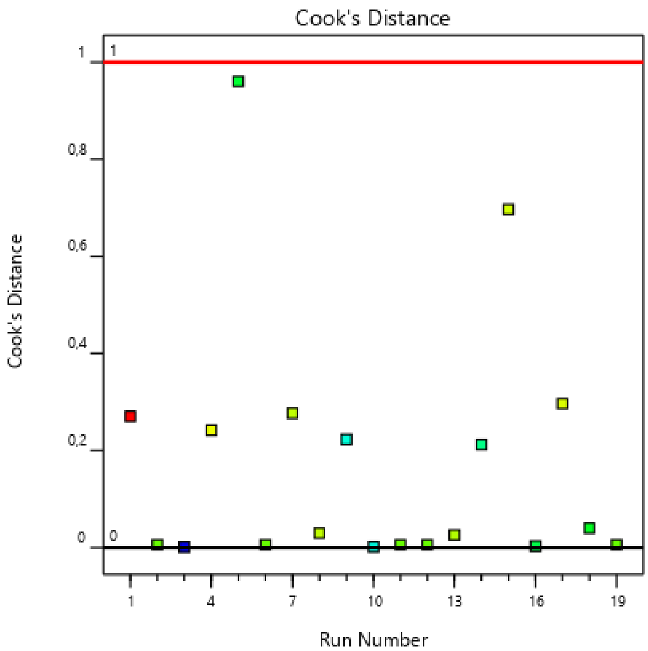

Figure 9 Run Number versus Cook's Distance (Deney Sayısı ile Cook's Mesafesi Karşılaştırılması)

3.2.6. Three Dimesional Interaction Graphics

The graphs in the Fgure 10-12 are three dimensional interaction graphs.

The relationship between conversion and temperature, amount of catalyst is seen in Figure 10.

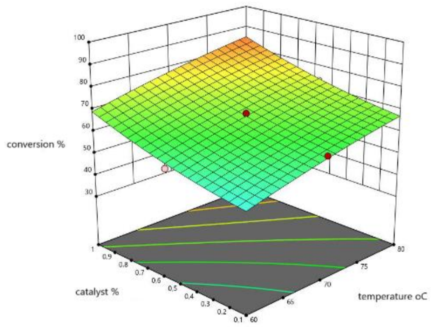

Figure 10 Three dimensional surface plots for effect of temperature and catalyst amount on conversion (Sıcaklık ve Katalizör Miktarı Dönüşüm İlişkisi Üç Boyutlu Grafiği)

When the three dimensional graph is examined in Figure 10, it is seen that the conversion increases with the temperature and the amount of catalyst.

The relationship between conversion and temperature, initial molar ratio is seen in Figure 11.

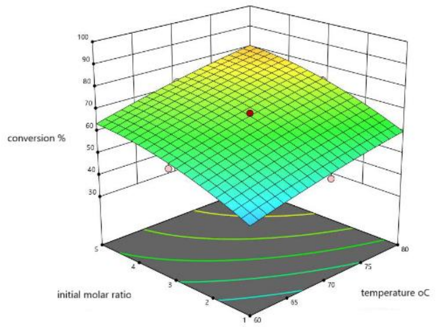

Figure 11 Three dimensional surface plots for effect of temperature and initial molar ratio on conversion (Sıcaklık ve Molar Oran Miktarı Dönüşüm İlişkisi Üç Boyutlu Grafiği)

The three-dimensional relationship between temperature, initial molar ratio and conversion is examined in Figure 11, it is seen that the conversion increases also with the increase in initial molar ratio and temperature.

The relationship between conversion and initial molar ratio, the amount of catalyst is seen in Figure 12.

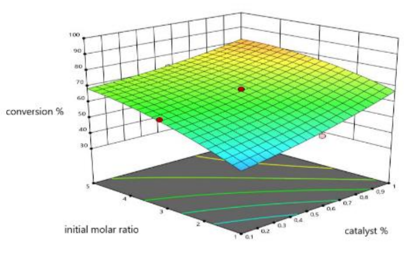

Figure 12 Three dimensional surface plots for effect of initial molar ratio and catalyst amount on conversion (Başlangıç Molar Oranı ve Katalizör Miktarı Dönüşüm İlişkisi Üç Boyutlu Grafiği)

Figure 12 is stated that the increase in the molar ratio and catalyst amount is the reason for the increase in the conversion values.

3.2.7. Optimum Values

At the end of the optimization that is made with the central composite design method in the program, the optimum operating conditions are given as 80 °C for the temperature, 1% for the catalyst amount and 5 for the initial molar ratio. The highest conversion value reached under these conditions is 89.35%. This value is the highest response value that can be obtained within 100 experiments given by the program. The desirability number for all data was seen as 1.

3.2.8. Importances of Factors

The limit values of the factors and their importance level on the response are given in Table 4.

Tablo 4 Limit Values of Factors and Importance of Factors on Response (Faktörlerin Limit Değerleri ve Yanıt Üzerinde Faktörlerin Önem Tablosu)

Factor name	Lower limit	Upper limit	Importance
A: Temperature °C	60	80	3
B: Catalyst amount %	0.1	1	3
C: Molar ratio	1	5	3
Response: Conversion %	35.7	90.2	3

In the program, both the effects of the temperature, the amount of catalyst, the initial molar ratio factors on the conversion and the importance levels of these factors on the response can also be determined as given in Table 4.

The effect of a factor on the response is defined as 1: little, 3: moderate, 5: much.

The importance levels were indicated that the effects of the factors on the response were moderate level.

4. Conclusion

It has been understood that as a result of the design made with the central composite design method by using the Design Expert program, the Quadratic model data are compatible with the actual data. Optimum conditions are 80 °C for temperature, 1% for catalyst amount and 5 for initial molar ratio. The highest conversion value at optimum conditions will be 89.35%. It has been understood that the factor that has the greatest effect on the response is the initial reactant molar ratio of the C factor. This is an known and expected result. One way to increase conversion in reversible reactions such as the esterification reaction is to use an excess of reactant. According to Le Chatelier's principle, the usage of excess reactant shifts the esterification reaction forward. The other way to increase the conversion in reversible reactions such as the esterification reaction is the withdrawal of water, the by-product formed. According to Le Chatelier's principle the withdrawal of water shifts the esterification reaction forward also. In this study, it has also been seen that the conversion values can be increased by sorping water with hydrogels. As the hydrogels capture water, the reaction shifts towards the product and the amount of ester increases. This technique is a much more economical way than using excess reactants for producing ester. No additional separation method may be required to separate the by-product water.

References

Aurand E. R., Lampe K. J., Kimberly B. Bjugstad K. B. (2013). Defining and Designing Polymers and Hydrogels for Neural Tissue Engineering. *Journal of Neuroscience Research*, 72 (3),199-213.

Bekdeşer, B. (2019). Modelling and Optimizing Microwave-Assisted Extraction of Antioxidants From Burdock (Arctium Lappa) Using Responce Surface Methodology. European Journal of Science and Technology, 17, 655-662.

Çolak M., Boyacı A., İ. (2018). A Fuzzy Logic Based Green Performance EvaluationModel for Automotive Industry . European Journal of Science and Technology, 13, 39-44.

Ezis, M. A., Ibrahim, V., Barakat, Y. (2018a). Effect of ethyl acetate addition on phase stability, octane number and volatility criteria of ethanol-gasoline blends. *Egyptian Journal of Petroleum*, 27 (4), 567-572.

Ezis, M. A., Awad, N., Ibrahim, V., Barakat, Y. (2018b). Influence of ethyl acetate addition on phase stability and fuel characteristics of hydrous ethanol-gasoline blends. *Egyptian Journal of Petroleum*, 27 (4), 1333-1336.

Fu X., Zhan Y., Meng Y., Li Y., Liao C., Lu Z. (2017).Graphene oxide/poly(vinyl alcohol) hydrogels with good tensile properties and reusable adsorption properties. *Plastics, Rubber and Composites*, 46,(2), 53–59.

Hasırcı, G., Hilmioğlu, N. (2018). Preparation and Usage of PVA/PAMPS Catalytic Membrane for Ester Production. *7 th National Catalysis Congress*, 17-18. Denizli, Turkey.

Hasırcı, G., İlgen, O., Hilmioğlu, N. (2019). Synthesis Of Solketal By Economic Catalyst Sulfo Succinic Acıd. *2nd International Conference on Life and Engineering Sciences*, 113-117. İstanbul, Turkey.

Hilmioğlu, N., Yılmaz, O, Ertürk, M. C. (2021). Optimization Of Ethyl Acetate Production By Response Surface Method, *Term Paper*, Kocaeli Üniversitesi, Kimya Mühendisliği Bölümü.

Hilmioğlu, N., Yenihan Yüzer, N., Hasırcı, G. (2020). Investigation Of The Effect Of Poly (Vinyl Alcohol) Hydrogel Particles On The Esterifications Reaction. *International Marmara Sciences Congress (Spring)*, 488-493. Kocaeli, Turkey.

Mok C. F., Ching C. Y., Muhamad F., Osman N. A. A., Hai N. D., Hassan C. R. C. (2020). Adsorption of Dyes Using Poly(vinyl alcohol) (PVA) and PVA-Based Polymer Composite Adsorbents: A Review. *Journal of Polymers and the Environment*, 28, 775–793.

Mortas, M., Awad, N. (2020). Optimization of Extraction Parameters by Response Surface Methodology in Handling Tea Extract From Fibrous Tea Waste. European *Journal of Science and Technology,* 20, 672-684.

Narasimhan, M., Muthukumaran, C., Sharmila, G. (2020). A comprehensive review on the application of response surface methodology for optimization of biodiesel production using different oil sources. *Journal of King Saud University - Engineering Science,* Article in press, Available online 29 September 2020. https://doi.org/10.1016/j.jksues.2020.09.012

Sirsam R., Hansora D., Usmani G. A. (2016). A Mini-Review on Solid Acid Catalysts for Esterification Reactions. *Journal of The Institution of Engineers (India): Series E*, 97 (2),167–181.

Soltani S., Rashid U. Al-Resayes S. I., Nehdi I. A. (2017). Recent progress in synthesis and surface functionalization of mesoporous acidic heterogeneous catalysts for esterification of free fatty acid feedstocks: A review. *Energy Conversion and Management*, 141, 183-205.

Turki, N., Boujelben, N., Bakari, Z., Bouzud, J. (2021). Use of Response Surface Methodology for Optimization of Nickel Adsorption in an Aqueous Solution by Clay. *American Journal of Environmental Sciences*, 2021, 17 (5) 92-100. DOI: 10.3844/ajessp.2021.92.100

Wang Y., Wang X., Xie Y., Zhang K.(2018). Functional nanomaterials through esterification of cellulose: a review of chemistry and application. *Cellulose*, 25, 3703–3731.

Yenihan Yüzer, N. , Hilmioğlu, N. (2019a). Diethyl Maleate Synthesis Wıth Hydrophilic Membrane Additive In The Batch Reactor. *International Marmara Science Sciences Congress* (Spring) , 1800-1806. Kocaeli, Turkey.

Yenihan Yüzer, N. (2019b). Membran Reaktörde İzopropil Asetat Üretiminin İncelenmesi, *Yüksek Lisans Tezi*, 40-42, Kocaeli Üniversitesi Fen Bilimleri Enstitüsü, Kimya Mühendisliği Anabilim Dalı.

Yüksel A. A. (2018), Utilization of Response Surface Methodology in Optimization of Extraction of Plant Materials. *Statistical Approaches With Emphasis on Design of Experiments Applied to Chemical Processes*. 2018, 157-169. DOI: 10.5772/intechopen.73690.