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Yield Prediction of Renewable Diesel From Hydrocracking Process as a Function of Pressure and Temperature Using Analytical Semi Empirical Model (ASEM)

Handrianto Wijaya[1], and *Bambang* Heru Susanto[1,*]

[1]Department of Chemical Engineering, University of Indonesia, 16424 Depok, Indonesia

Abstract. The development of renewable fuels from biomass is very rapid, and becomes the main alternative to replace petroleum-derived fuels that are limited in stock. There has been a lot of experiments to optimize the production of renewable diesel, but it takes time, cost and a lot of trial and error in order to produce a good result. On the other hand, optimization using simulation is more cost and time effective. One of the processes in the production of this renewable fuel is hydrocracking. This experiment aims to study the effect of pressure and temperature in the hydrocracking process using the Analytical Semi Empirical Model (ASEM) method in representing the yield of the product. Mathematical models will be modified and validated using data from existing research. The results show that Analytical Semi Empirical Model can be used to predict the yield of product from hydrocracking, with all of the models show R^2 higher than 0.95 and SSE lower than 3.

1 Introduction

The use of renewable fuel to replace the conventional fuel has been a common thing. There has been a lot of research done in order to optimize the production, effectivity and the usage of renewable fuel, in hope that someday, it will completely replace the conventional fuel. One of the research to improve the production of renewable fuel is the use of Analytical Semi Empirical Model (ASEM) in order to predict the yield and optimum operating conditions in the production process.

1.1 Analytical Semi Empirical Model

The Analytical Semi Empirical Model (ASEM) is a combination of empirical and analytical method, in which, both of the elements presents in this model, and thus can be called "in between" the empirical and analytical models. The empirical model plays role as the base of the semi empirical model, and it will further be modified in order to get the semi empirical model. The modification of the empirical models heavily relies to analytical method: the trial and error.

The Analytical Semi Empirical Model was first introduced by Green to predict the yield from pyrolysis. The model is made from the learning curve and forgetting curve, in which shows the trend of the yield. [1] The learning curve shows the tendency of the yield to raise as the variable raises, on the other hand, the forgetting curve shows the tendency of the yield to decline as the variable raises. The analytical semi empirical model consists of both concept, and mathematically can be written as follows:

$$Y(T) = W[L(T)^p\,[F(T)]^q \quad (1)$$

$$L(T) = 1/[1+exp\ Z] \quad (2)$$

$$Z = (T_0 - T)/D \quad (3)$$

$$F(T) = 1\text{-}L(T) \quad (4)$$

With $Y(T)$ is yield as a function of temperature; W is the yield parameter; $L(T)$ and $F(T)$ are the learning curve and forgetting curve respectively, as a function of temperature; p and q is the constant in Eq. (1); D is parameter of logistic function from Eq. (1).

The analytical semi empirical model has been used in several other experiments to predict the yield of the product from some process, such as pyrolysis, [1-2] thermal cracking [3] and catalytic cracking [4], in which the three are a function of temperature only. There is another experiment to express ASEM as a function of temperature and time for thermal cracking, but there hasn't been a model that is a function of both temperature and pressure. [5] This experiment aims to produce an equation which can be used to predict yield as a function of temperature and pressure, as in hydrocracking process.

1.2 Hydrocracking Process

Hydrocracking process is a combination of catalytic cracking and hydrogenation, in which heavy fraction is cracked with the help of hydrogen to produce lighter fraction product. This process operates on high temperature and pressure, needs catalyst and hydrogen.

* Corresponding author: bambanghs@che.ui.ac.id

Hydrocracking is categorized under the hydrotreatment process. As a part of hydrotreatment process, typical reactions that occurs within hydrocracking process includes decarboxylation, decarbonylation and hydrodeoxygenation. The decarbonylation process is also divided into two type, based on whether a catalyst's presence: thermal reaction, which doesn't require catalyst to occur; and catalytic reaction, which needs catalyst to occur. [6]

As temperature rises, side reactions may occur. These side reactions will reduce the yield value, and the prevention is one of the main focus in industry. Typical side reactions that may occur includes the reverse water gas shift and methanation. On decarboxylation process, as temperature rises, first side reaction (reverse water gas shift) occurs, and until certain point of temperature, methanation occurs. On decarbonylation process, the only side reaction that may occurs is methanation. [6-7].

2 Experimental

Eq. (5) shows the ASEM as a function of temperature only, which is developed by Green. [1-3].

$$Y(T)= W\{1/1+exp[(T_0-T)/D]\}^p\{1/1+exp[(T-T_0)/D]\}^q \quad (5)$$

With W being a parameter of logistic function, which is related to the maximum value of yield that can be achieved from the reaction; D is a parameter of logistic function, which fixes the slope of the curve. Both the value can be adjusted so that the curve fits the data used.

The modification for the model is carried out by adding variable pressure to the model. Modelling starts with finding the right mathematic equation to express the correlation between pressure and yield. The mathematic equation is then derived to form an equation which describes the correlation between yield and pressure. The semi empirical model for thermal cracking is then modified by adding the variable pressure to the model, based on the correlation. The modified model is then validated using data from various sources by curve fitting method, and is being analysed to see whether the model can be used to predict yield from hydrocracking process by calculating the R^2 and SSE from each simulation. If the results' R^2 <0.95 and SSE > 3, the parameter(s) within the model (D, and/or W) will have to be re-adjusted so that the results' R^2 > 0.95 and SSE < 3.

The mathematical model was derived from mass balance.

$$In – Out + Generation = Accumulation \quad (6)$$

$$k(W-Y) + 0 = dY/dt \quad (7)$$

$$r(W-Y) = dY/dt \quad (8)$$

$$\int r\, dt = \int dy/(W-Y) \quad (9)$$

It is known that changes in pressure over time will affect the Henry constant. The Henry equation can be written as follows:

$$P = H \times C \quad (10)$$

Concentration in the Eq. (9) can be substituted, so that Eq. (9) becomes the function of time, as follows:

$$dP = H \times r\, dt \quad (11)$$

$$dP/H = r\, dt \quad (12)$$

Substituting Eq. (11) to Eq. (8) will result in the following equation.

$$\int dP/H = \int dy/(W-Y) \quad (13)$$

$$1/H \int dP = \int 1/(W-Y)\, dy \quad (14)$$

$$P/H = \ln (W-Y)/Y \quad (15)$$

$$\exp (P/H) = W/Y – 1 \quad (16)$$

$$Y = W (1/1+exp(P/H)) \quad (17)$$

Eq. (17) shows the correlation between Y, P, and H. The semi empirical model becomes:

$$Y(T,P)=W\{1/1+exp[T(P_0-P)/DH]\}^p\{1/1+exp[T(P-P_0)/DH]\}^q \quad (18)$$

$$Y(T,P)=W\{1/1+exp[P(T_0-T)/D]\}^p\{1/1+exp[P(T-T_0)/D]\}^q \quad (19)$$

Eq. (18) is the semi empirical model for when the temperature remains constant and pressure changes over time, while Eq. (19) is the semi empirical model at pressure remains constant and temperature changes over time. Temperature effects on Henry Constant (H) is assumed to be negligible, therefore leads to Eq. (19). Eq. (19) shows similarity to Eq. (5), which is a model proposed by Green [1-3]. When the value of P equals 1 atm (atmospheric), P effect on yield (Y) is negligible and thus leading back to Eq. (5).

3 Results and Discussions

The simulation of ASEM is carried out through Curve Fitting Toolbox from MATLAB using secondary data from various sources, as shown in the following table.

Table 1. Summary of Data Used in Experiment

Case	Summary of Data	Raw Material
1	Sunflower Oil Hydrocracking at 380°C [8]	Sunflower Oil
2	Rapeseed Oil Hydrocracking at 350°C [9]	Rapeseed Oil
3	Soybean Oil Hydrocracking at 10 MPa [10]	Soybean Oil
4	Canola Oil Hydrocracking at 9 MPa [11]	Canola Oil

3.1 Results

The simulation of ASEM in Eq. (18) used Case 1 and 2's data (pressure variation), while Eq. (19) used Case 3 and 4's data (temperature variation).

Case 1 uses data of C-17 and C-18 at 380°C at 40-80 bar. The result of simulation shows SSE value of 7.8E-19 and R^2 = 1. The fitting curve is shown in Fig. (1).

Simulation for Case 2 uses yield data of C-17 and C-18 at 350°C, 8-10 MPa with Ni-Mo/γ-Al_2O_3. The result of the simulation shows SSE for C-17's curve =

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0.0345 with R^2 = 0.99; and SSE for C-18's curve = 7E-15 with R^2 = 1. The fitting curve is shown in Fig. (2).

Fig. (3) shows the result of Case 1's simulation. The simulation is done using data of C-17's yield at 240-280°C, 10 MPa. The simulation shows a fit between the data and the fitting curve using Eq. (19), with SSE = 3.82E-22 and R^2 = 1, as shown in Fig. (3).

Simulation for Case 4 uses data of C-17 and C-18's yield, at 350-400°C, 9 MPa, using Ni-Mo/γ-Al_2O_3. Simulation's result also shows a fit between the data and the fitting curve, with SSE for C-17's curve = 5.71E-25; SSE for C-18's curve = 2.98E-16; R^2 for both curve = 1. as shown in Fig. (4).

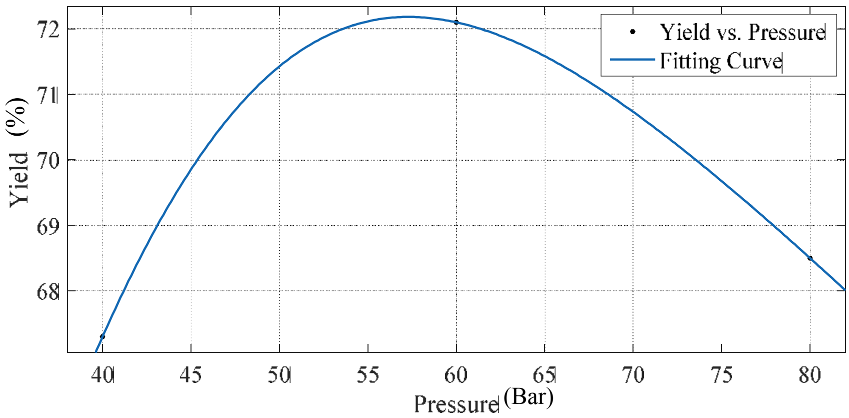

Fig. 1. Curve Fitting Result for Case 1

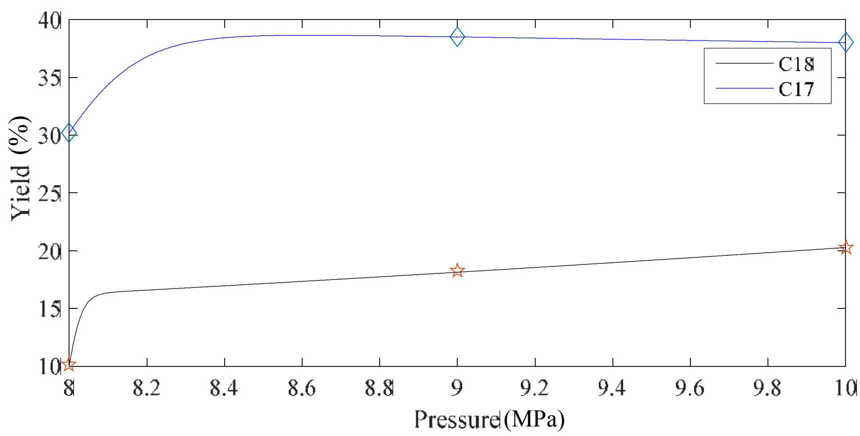

Fig. 2. Curve Fitting Result for Case 2

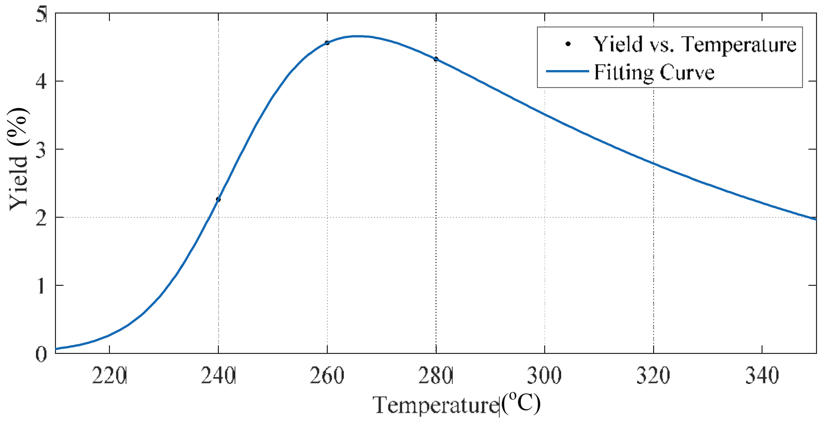

Fig. 3. Curve Fitting Result for Case 3

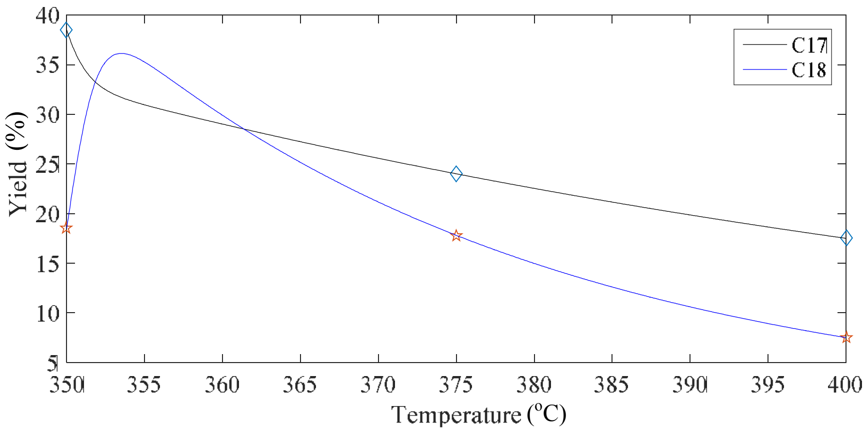

Fig. 4. Curve Fitting Result for Case 4

Parameters from ASEM model used for simulations are shown and summary of SSE and R^2 for each cases are show in table 2 below.

Table 2. Simulation Parameters

Case	Parameters					*Goodness of fit*	
	W	**T_i**	**D**	**P**	**Q**	**SSE**	**R^2**
1	81	60	100	0.2	0.04	7.8E-19	1
2	16.2	8	50	0.7	-0.002	0.0345	0.99
	39	8	50	0.4	0.0015	7E-15	1
	W	**P_i**	**D**	**P**	**Q**	**SSE**	**R^2**
3	7.1	240	100	1.5	0.12	3.8E-22	1
4	32.9	350	10	-0.2	0.01	5.7E-25	1
	42.3	350	10	1.2	0.03	2.9E-26	1

Additionally, the optimum temperature and pressure to achieve maximum value of yield from each case can be determined from the simulation's results. Table 3 shows the optimum conditions (temperature and pressure) and comparisons to data sources' optimum conditions.

Table 3. Optimum Conditions Based on Simulation's Results & Data Sources

Case	Optimum Condition (Based on Source)	Optimum Condition (Based on Simulation)
1	60 Bar	56.53 Bar
2	10 MPa (n-C17) 9 MPa (n-C18)	10 MPa (n-C_{17}) 8.58 MPa (n-C_{18})
3	260°C	265.2°C
4	350°C (n-C_{17} & n-C_{18})	350°C (n-C_{17}) 353.57°C (n-C_{18})

3.2 Discussion

Upon validating ASEM for temperature variation, parameter *D* was adjusted so that the curve fits the source data. On the other hand, upon validating ASEM for pressure variation, parameter *W* and *D* were adjusted so that the curve fits the data. The value of *D* is assumed to be the same in learning curve and the forgetting curve. The value of *p* and *q* represents the tendency of the yield to raise and decline respectively as the variable (temperature and pressure) raises over time. The value of $p > 1$ represents slow learning, whereas $p < 1$ represents fast learning. The same can be said for parameter *q*, in which $q > 1$ represents slow declining and $q < 1$ represents fast declining.

In general, the use of ASEM to predict yield as a function of temperature only is as simple as; if not simpler than conventional method, which includes the making of log *Y* vs log 1/*T* curve, Boltzmann integrals, kinetic equations, and other numerical approaches. However, when the yield is treated as a function of both temperature and pressure, the yield prediction by using numerical method becomes harder and might take a lot of time to solve.

ASEM method assumes that other factors besides the main variable(s) are negligible, which makes calculation simpler than the conventional method.

The results of simulations show that the value of SSE < 3 and R^2 > 0.95. These results show that the ASEM model proposed in this experiment can be used to predict the yield of renewable diesel from hydrocracking various raw materials, even with varying kind of catalyst, operation condition and raw materials.

From the simulations, one can also determine the optimum conditions for each cases. The optimum condition is easily achieved from the curve, by using the data point tool from curve fitting curve. The optimum conditions from simulation have the almost same value, if not, the exact same value as the one from the data, thus being one of the advantages of using ASEM method.

The simulation also gives the value of Henry's constant (H), however, the value of H cannot be validated, since there isn't any data for Henry's constant in specific temperature and pressure, moreover for reactions with high temperature and high pressure.

4. Conclusion

The results show that Analytical Semi Empirical Model can be used to predict the yield of product from hydrocracking, with all of the models show R^2 higher than 0.95 and SSE lower than 3. Based on the simulation results, it can be concluded that the ASEM models used in this experiment can be used to predict yield of renewable diesel from various raw materials. It can also be concluded that the ASEM model can be used to determine the optimum conditions for each case.

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