

APPENDIX A

COMPOSITION OF PALM OIL

The composition below is obtained using GCMS-QP2010S SHIMADZU.

Column : Rtx-5MS

Length : 30 meter

ID : 0.25 mm

Table A.1.	The	Com	position	of Pa	lm Oil
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Component	Composition (%)
Dodecanoic acid $(C_{13}H_{26}O_2)$	0.5
Tetradecanoic acid $(C_{15}H_{30}O_2)$	1.28
Hexadecenoic acid $(C_{17}H_{32}O_2)$	0.18
Hexadecanoic acid $(C_{17}H_{34}O_2)$	39.28
Heptadecanoic acid $(C_{18}H_{36}O_2)$	0.09
Octadecenoic acid $(C_{19}H_{36}O_2)$	53.54
Octadecanoic acid (C ₁₉ H ₃₈ O ₂)	4.67
Eicosenoic acid $(C_{21}H_{40}O_2)$	0.14
Eicosanoic acid $(C_{21}H_{42}O_2)$	0.32

APPENDIX B

LIQUID PRODUCT

The data of the liquid product obtained in this experiment are presented in Table B.1, Table B.2, and Table B.3 for reaction temperature of 623.15 K, 673.15 K, and 723.15 K respectively.

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WHSV (hr ⁻¹)	15	17.5	20	22.5	25	27.5	30				
Liquid product											
(gram)	27.2415	27.9923	28.4245	28.6845	28.9023	29.5523	29.8805				

Table B.1. Liquid Product's Mass for Reaction Temperature of 623.15 K

Table B.2. Liquid Product's Mass for Reaction Temperature of 673.15 K

WHSV (hr ⁻¹)	15	17.5	20	22.5	25	27.5	30
Liquid product							
(gram)	25.909	26.0423	26.4128	26.6013	27.0595	27.3423	27.9305

Table B.3. Liquid Product's Mass for Reaction Temperature of 723.15 K

WHSV (hr ⁻¹)	15	17.5	20	22.5	25	27.5	30
Liquid product							
(gram)	25.6783	25.9968	26.1495	26.5558	26.949	27.3065	27.7128

APPENDIX C

CONCENTRATION DATA FOR VARIOUS WHSV AND REACTION TEMPERATURES

The concentration data for various WHSV and reaction temperatures of 623.15 K, 673.15 K, and 723.15 K are presented in the mass percent and shown in Table C.1, Table C.2, and Table C.3 respectively.

Table C.1. Concentration Data for Reaction Temperature of 623.15 K

WHSV (hr ⁻¹)	15.0	17.5	20.0	22.5	25.0	27.5	30.0
C _P (% wt)	49.12%	53.01%	57.34%	60.13%	63.12%	66.81%	70.71%
C _{OLP} (% wt)	34.70%	33.12%	30.12%	28.13%	25.81%	24.12%	21.23%
C _{gas+coke} (% wt)	16.18%	13.87%	12.54%	11.74%	11.07%	9.07%	8.06%

Table C.2. Concentration Data for Reaction Temperature of 673.15 K

WHSV (hr ⁻¹)	15.0	17.5	20.0	22.5	25.0	27.5	30.0
C _P (% wt)	21.92%	24.13%	29.13%	33.85%	38.13%	40.12%	46.13%
C _{OLP} (% wt)	57.80%	56.00%	52.14%	48.00%	45.13%	44.01%	39.81%
C _{gas+coke} (% wt)	20.28%	19.87%	18.73%	18.15%	16.74%	15.87%	14.06%

Table C.3. Concentration Data for Reaction Temperature of 723.15 K

WHSV							
(hr ⁻¹)	15.0	17.5	20.0	22.5	25.0	27.5	30.0
C _P (% wt)	13.01%	15.98%	18.34%	22.59%	25.80%	28.12%	32.68%
C _{OLP}							
(% wt)	66.00%	64.01%	62.12%	59.12%	57.12%	55.90%	52.58%
Cgas+coke							
(% wt)	20.99%	20.01%	19.54%	18.29%	17.08%	15.98%	14.73%

APPENDIX D

CALCULATION OF FLOW RATE OF THE PALM OIL AND

MAXIMUM RUN TIME

WHSV is defined as:

WHSV
$$(h^{-1}) = \frac{\text{flow rate of oil (gram/h)}}{\text{mass of catalyst (gram)}}$$
 (D.1)

Since the mass of catalyst used is 1 gram, hence the value of the flow rate of liquid oil would be the same as the WHSV. Also, the maximum amount of palm oil possible to be cracked is 1/(C/O) or O/C grams (oil to catalyst ratio). So the maximum run time would be:

Example:

Mass of catalyst	: 1 gram
Total oil	: 32.5 gram
WHSV	: 15/h
Flow rate of oil	: 15 gram/h
Maximum run time	: 2.1667 h (130 min)

APPENDIX E

ALGORITHM OF GAUSS-JORDAN METHOD USING MATLAB

7.1 PROGRAM

```
f=input('Put the data in the form of matrixes =')
[a,b]=size(f)
t=1
while t \sim = (b-1)
u=f(:,t)
s=u(t:a)
v=max(s)
[r,k]=find(v==u)
g=f(r(1),:)
h=f(t,:)
f(t,:)=g
f(r(1),:)=h
for
      li=t+1:a
      j=t:b
      f(i,j) = f(i,j) - f(i,t) / f(t,t) * f(t,j)
end
t=t+1
end
n=t
d(n) = f(n, n+1) / f(n, n)
for
      i=(n-1):-1:1
      j=(i+1):n
      d(i) = (f(i, n+1) - sum(f(i, j) . * d(j))) / f(i, i)
end
```

APPENDIX F

ALGORITHM OF RUNGE-KUTTA METHOD USING MATLAB

7.1 PROGRAM

```
t=0
x=1 % CP
y=0 % COLP
z=0 % Cgas+coke
h=.001
k1=input('input k1value=')
k2=input('input k2value=')
k3=input('masukkan k3value=')
tmax=input('masukkan tmax value=')
k1x=h*(k1+k2)*x
k1y=h*(k1*x-k3*y)
k1z=h*(k2*x+k3*y)
k2x=h*(k1+k2)*(x+0.5*k1x)
k2y=h*(k1*(x+0.5*k1x)-k3*(y+0.5*k1y))
k2z=h*(k2*(x+0.5*k1x)+k3*(y+0.5*k1y))
k3x=h*(k1+k2)*(x+0.5*k2x)
k3y=h*(k1*(x+0.5*k2x)-k3*(y+0.5*k2y))
k3z=h*(k2*(x+0.5*k2x)+k3*(y+0.5*k2y))
k4x=h*(k1+k2)*(x+k3x)
k4y=h*(k1*(x+k3x)-k3*(y+k3y))
k4z=h*(k2*(x+k3x)+k3*(y+k3y))
while t<tmax
      t=t+h
      x=x+(k1x+2*k2x+2*k3x+k4x)/6
      y=y+(k1y+2*k2y+2*k3y+k4y)/6
      z=z+(k1z+2*k2z+2*k3z+k4z)/6
      k1x=h*(k1+k2)*x
      k1y=h*(k1*x-k3*y)
      k1z=h*(k2*x+k3*y)
      k2x=h*(k1+k2)*(x+0.5*k1x)
      k2y=h*(k1*(x+0.5*k1x)-k3*(y+0.5*k1y))
      k2z=h*(k2*(x+0.5*k1x)+k3*(y+0.5*k1y))
      k3x=h*(k1+k2)*(x+0.5*k2x)
      k_{3y=h*}(k_{1*}(x+0.5*k_{2x})-k_{3*}(y+0.5*k_{2y}))
```

```
k3z=h*(k2*(x+0.5*k2x)+k3*(y+0.5*k2y))
k4x=h*(k1+k2)*(x+k3x)
k4y=h*(k1*(x+k3x)-k3*(y+k3y))
k4z=h*(k2*(x+k3x)+k3*(y+k3y))
```

end

APPENDIX G

CALCULATION METHOD

1. Calculation Method Used for Determining the Concentration of UPO, OLP, and Gas + Coke

The data obtained in this experiment are the total volume of the liquid product and the mass of the coke. However, the data of the coke's mass were not necessarily used in the calculation. The liquid product obtained in this experiment were a mixture of hydrocarbons, consists of the long chain hydrocarbons from the palm oil and the short chain hydrocarbons as a result of the catalytic cracking reaction. The long chain hydrocarbons known as the unconverted palm oil and the short chain hydrocarbons known as the organic liquid product. To determine the amount of those components, the liquid product was then analyzed using GC.

The result of the GC analysis was the retention time and the area of each component contained in the liquid product. The area of each component was assumed to be the percent mass of each component in the mixture. This result was compared with those of the palm oil. The component which had the similar retention time with those of the palm oil's component was assumed to be the component of the palm oil, thus it was classified as the unconverted palm oil (UPO). The rest of it was considered as the result of the cracking reaction that is the organic liquid product (OLP). Therefore, the percent mass of the UPO and the OLP in the liquid product could be obtained.

The liquid product was also weighed to obtain its mass. The concentration, in percent mass, for UPO (C_P), OLP (C_{OLP}), and gas+coke ($_{Cgas+coke}$) was determined using equations as follow.

mass of UPO =
$$\frac{\text{area of UPO}}{\text{total area of liquid product}} \times \text{mass of liquid product}$$
 (G.1)

mass of
$$OLP = \frac{\text{area of } OLP}{\text{total area of liquid product}} \times \text{ mass of liquid product}$$
 (G.2)

$$C_{p} = \frac{\text{mass of UPO}}{\text{total mass of palm oil}} \times 100\%$$
(G.3)

$$C_{OLP} = \frac{\text{mass of OLP}}{\text{total mass of palm oil}} \times 100\%$$
(G.4)

$$C_{gas+coke} = 100\% - C_P - C_{OLP}$$
(G.5)

2. Calculation Method Used for Determining the Rate Constants

The concentration data in Table C.1, Table C.2, and Table C.3 were used to determine whether the catalytic cracking reaction of the palm oil follows the first order kinetic or the second order kinetic. The data were plotted into a chart based on both kinetics. If the cracking reaction was assumed to be a first order reaction, then equation II.4-2 was used. On the other hand, if the cracking reaction followed the second order kinetic, the equation II.4-4 was used. The plot of both chart were supposed to give a straight line, and thus the linear regression could be used to determine the value of the slope and the intercept of the plot. To determine the kinetic order of the cracking reaction, the R^2 value of those charts were compared to decide which one has a better value. From the concentration data obtained in this experiment, it was found that the cracking reaction follows the first order kinetic. The charts of both kinetics are presented in Figure G.1 for reaction temperature of 623.15 K, Figure G.2 for reaction temperature of 673.15 K, and Figure G.3 for reaction temperature of 723.15 K.



Figure G.1. Charts of First Order Kinetic and Second Order Kinetic for

Reaction Temperature of 623.15 K





Figure G.2. Charts of First Order Kinetic and Second Order Kinetic for

Reaction Temperature of 673.15 K

0,03

0,04



Figure G.3. Charts of First Order Kinetic and Second Order Kinetic for **Reaction Temperature of 723.15 K**

0,06

0,07

From those figures above, it could be concluded that the catalytic cracking reaction was a first order reaction. Therefore, the slope of those first order charts were the value of $-(k_1 + k_2)$ for each reaction temperature and the equations used for calculating the rate constants were equation II.4-5 and II.4-6. Equation II.4-5 and II.4-6 were solved using the least-square method.

For equation II.4-5, the least-square methods used for solving this equation were:

$$a.n+k_1.\sum Cp-k_3.\sum C_{OLP} = \sum \frac{dC_{OLP}}{d\tau}$$
(G.6)

$$a \sum C_p + k1 \sum C_p^2 - k_3 \sum (C_{OLP} C_p) = \sum \left(\frac{dC_{OLP}}{d\tau} C_p\right)$$
(G.7)

$$a \sum C_{OLP} + k_l \sum C_p C_{OLP} - k_3 \sum C_{OLP}^2 = \sum \left(\frac{dC_{OLP}}{d\tau} . C_{OLP} \right)$$
(G.8)

The value of C_P and C_{OLP} used to solve these equations were taken directly

from Table C.1, Table C.2, and Table C.3. As for the value of $\frac{dC_{OLP}}{d\tau}$, a plot of C_{OLP} and τ were made. The plot was assumed to be a second order polynomial and the equation that represents the plot could be known. This equation was differentiated to obtain the equation for $\frac{dC_{OLP}}{d\tau}$. So, the value of $\frac{dC_{OLP}}{d\tau}$ for each τ could be determined by using the differentiated equation. Charts of C_{OLP} and τ for different reaction temperature are presented in Figure G.4.



MODELLING OF LIQUID FUEL PRODUCTION VIA CATALYTIC CRACKING OF PALM OIL USING MCM-41 AS CATALYST

SURABAYA



Figure G.4. Plot of C_{OLP} and τ for Different Reaction Temperature

Using Gauss-Jordan method with Mathlab 7.1 program (Appendix E), the value of the rate constants k_1 and k_3 for each temperature are obtained. Aside from the value of the rate constants, the value of constant *a* can also be found. However, since the value of constant *a* is relatively small compared to the value of the rate constants, it can be neglected without affecting the value of k_1 and k_3 .

- k_{II} = the k_I value for the temperature 623.15 K
- k_{12} = the k_1 value for the temperature 673.15 K
- k_{I3} = the k_I value for the temperature 723.15 K

 k_{31} = the k_3 value for the temperature 623.15 K

 k_{32} = the k_3 value for the temperature 673.15 K

 k_{33} = the k_3 value for the temperature 723.15 K

For equation 11.4-6, the least-square methods used for solving this equation were:

$$a.n+k_2.\Sigma Cp+k_3.\Sigma C_{OLP} = \Sigma \frac{dC_{gas+coke}}{d\tau}$$
(G.9)

$$a \sum C_p + k_2 \sum C_p^2 + k_3 \sum (C_{OLP} C_p) = \sum \left(\frac{dC_{gas+coke}}{d\tau} C_p\right)$$
(G.10)

$$a \sum C_{OLP} + k_2 \sum C_p C_{OLP} + k_3 \sum C_{OLP}^2 = \sum \left(\frac{dC_{gas+coke}}{d\tau} . C_{OLP} \right)$$
(G.11)

The value of C_P and C_{OLP} used to solve these equations were taken directly from Table C.1, Table C.2, and Table C.3. As for the value of $\frac{dC_{gas+coke}}{d\tau}$, a plot of $C_{gas+coke}$ and τ were made. The plot was assumed to be a second order polynomial and the equation that represents the plot could be known. This equation was differentiated to obtain the equation for $\frac{dC_{gas+coke}}{d\tau}$. So, the value of $\frac{dC_{gas+coke}}{d\tau}$ for each τ could be determined by using the differentiated equation. Charts of $C_{gas+coke}$ and τ for different

reaction temperature are presented in Figure G.5.

3. Calculation Method Used for Determining the Activation Energy

The activation energy for each reaction was calculated using the Arrhenius equation. The Arrhenius equation is defined as follows:

$$\ln(k_n) = \ln(k_{n0}) - \frac{E_n}{RT}$$
(G.11)

To solve this equation, the rate constant values for each reaction temperature were plotted against 1/T (reaction temperature) to give a straight line with a slope equal to $\begin{pmatrix} -E_n \\ R \end{pmatrix}$ and intercept equal to $\ln (k_{n0})$. Therefore, from this equation, the value of activation energy for each reaction (E_n) and the Arrhenius constant (k_{n0}) could be determined. The plot obtained from the Arrhenius equation is presented in Figure G.6.



Figure G.6. Plot of Arrhenius Equation

4. Calculation Method Used for Determining the Predicted Data

The predicted data is calculated using Runge-Kutta numerical method. The algorithm for Runge- Kutta numerical method used in Mathlab 7.1 program is shown in Appendix F.

APPENDIX H

PREDICTED CONCENTRATION DATA FOR VARIOUS WHSV

AND REACTION TEMPERATURES

The predicted concentration data for various WHSV and reaction temperatures of 623.15 K, 673.15 K, and 723.15 K, obtained using Runge-Kutta algorithm shown in Appendix F, are presented in the mass percent and shown in Table H.1, Table H.2, and Table H.3 respectively.

 Table H.1. Predicted Data for Reaction Temperature of 623.15 K

WHSV (hr ⁻¹)	15.0	17.5	20.0	22.5	25.0	27.5	30.0
C _P (% wt)	52.10 %	55.28%	58.39 %	63.24 %	64.92 %	69.33 %	74.01 %
C _{OLP} (% wt)	34.13 %	32.01 %	29.13 %	26.12 %	25.14 %	22.12 %	17.91 %
C _{gas+coke} (% wt)	13.77 %	12.71 %	12.48 %	10.64 %	9.94 %	8.55 %	8.08 %

Table H.2. Predicted Data for Reaction Temperature of 673.15 K

WHSV (hr ⁻¹)	15.0	17.5	20.0	22.5	25.0	27.5	30.0
C_{P} (% wt)	23.12 %	25.13 %	28.13 %	32.12 %	37.89 %	39.8 %	48.31 %
C _{OLP} (% wt)	58.09 %	56.91 %	55.01 %	51.12 %	47.31 %	45.41 %	39.41 %
C _{gas+coke} (% wt)	18.79 %	17.96 %	16.86 %	16.76 %	14.8 %	14.79 %	12.28 %

Table H.3. Predicted Data for Reaction Temperature of 723.15 K

WHSV (hr ⁻¹)	15.0	17.5	20.0	22.5	25.0	27.5	30.0
C_{P} (% wt)	14.2 %	17.21 %	19.21 %	23.41 %	26.91 %	29.13 %	33.12 %
C _{OLP} (% wt)	67.14 %	65.41 %	63.41 %	60.13 %	58.12 %	56.41 %	53.21 %
C _{gas+coke} (% wt)	21.8 %	21.41 %	20.12 %	19.51 %	18.71 %	16.41 %	15.61 %