第 49 卷 第 2 期
2022 年 2 月

湖南大学学报（自然科学版）
Journal of Hunan University (Natural Sciences）

Vol. 49 No. 2
February 2022

Open Access Article https://doi.org/10.55463/issn.1674-2974.49.2.12

Distillation of Pyrolysis Results from Mixed Used Plastic and Palm Oil in The Fractionation Column to Produce the Gasoline Fraction, with RON Analysis: Experiments and Modeling

Atha Pahlevi [1], Ali Altway [1], Orchidea Rachmaniah[1], Agus Slamet[2], Tri Widjaja[1*]

[1] *Department of Chemical Engineering, Sepuluh Nopember Institute of Technology, Surabaya, East Java, Indonesia*

[2] *Department of Civil Engineering, Sepuluh Nopember Institute of Technology, Surabaya, East Java, Indonesia*

Abstract: Reprocessing plastic waste to become fuel oil is a good process. Plastics were originally obtained from the polymerization of petroleum products. According to SIPSN data from the Ministry of Environment in 2020, plastic waste in Indonesia has reached 17.314 million tons/year. In addition to using recycling, reduction can be made using hydrothermal pyrolysis cracking to convert solid plastic waste into liquid gasoline fractions with the help of co-reactants. However, with the pyrolysis process, the final result of the process allows the presence of impurities that are still contained in it. In this research, the distillation of the pyrolysis results for gasoline fraction plastic waste was carried out using a fractionated distillation column. The distillation process enhances the performance of petroleum oil with an average of RON 98 and a caloric value of 10,609,7 cal/gr. Modeling and simulation using excel of the distillation results of pyrolysis were carried out, it was found that the increase in the reflux ratio led to an increase in the purity of the distillation product and the effect of residence time caused the longer the process to run, the lower the distillation product. Therefore, the separation should not be done too long, which can cause the purity to decrease every time. The higher the reflux ratio, the smaller the kinematic viscosities get proven by experimental and modeling, but the value is a striking difference due to deviation from the model.

Keywords: distillation, RON, modeling, pyrolysis.

分馏塔中混合废塑料和棕榈油的热解结果蒸馏以生产汽油馏分，辛烷值 分析：实验和建模

摘要：将塑料废料再加工成燃料油是一个很好的过程。塑料最初是从石油产品的聚合中获得的。根据环境部 2020 年国家信息系统数据，印尼塑料垃圾已达 1731.4 万吨/年。除了使用回收之外，还可以使用水热裂解裂解在共反应物的帮助下将固体塑料废物转化为液体汽油馏分进行还原。然而，对于热解过程，该过程的最终结果允许存在仍然包含在其中的杂质。在这项研究中，使用分馏塔对汽油馏分废塑料的热解结果进行蒸馏。蒸馏过程提高了石油的性能，平均 辛烷值 98 和 10,609,7 卡路里/克的热值。使用擅长对热解的蒸馏结果进行建模和模拟，发现回流比的增加导致蒸馏产物纯度的提高，停留时间的影响导致过程运行的时间更长，蒸馏产物越低。因此，分离时间不宜过长，否则会导致纯度每次下降。回流比越高，通过实验和建模证明的运动粘度越小，但由于与模型的偏差，该值存在显着差异。

关键词：蒸馏，辛烷值，建模，热解。

Received: November 30, 2021 / Revised: December 29, 2021 / Accepted: January 10, 2022 / Published: February 28, 2022

Fund Project: 1177/PKS/ITS/2021 Ministry of Research and Technology/National Agency for Research and Technology

About the authors: Atha Pahlevi, Ali Altway, Orchidea Rachmaniah, Tri Widjaja, Department of Chemical Engineering, Sepuluh Nopember Institute of Technology, Surabaya, Indonesia; Agus Slamet, Department of Civil Engineering, Sepuluh Nopember Institute of Technology, Surabaya, Indonesia

Corresponding author Tri Widjaja, triw@chem-eng.its.ac.id

1. Introduction

The large population of Indonesia causes Indonesia's high energy needs. According to data from the National Development Planning Agency (Bappenas), Indonesia's population in 2019 reached 267 million and will increase every year.

The increase in energy demand is not proportional to existing energy reserves. According to data from the Ministry of Energy and Mineral Resources (ESDM), the number of oil reserves in Indonesia in 2019 only reached 3.2-3.3 billion barrels. With the current production level of 803 thousand barrels/day, these reserves will only last for 9 years ahead. Reprocessing plastic waste to become fuel oil is a promising process among the alternative energies being developed. Plastics were originally obtained from the polymerization of petroleum products. According to SIPSN data from the Ministry of Environment in 2020, plastic waste in Indonesia has reached 17.314 million tons/year. In addition to using recycling, reduction can be made using hydrothermal pyrolysis cracking to convert solid plastic waste into liquid gasoline fractions with the help of co-reactants. The advantage of the pyrolysis process, it can produce alternative fuel [1, 2]. The use of a catalyst in the pyrolysis process can increase the production of the gasoline fraction from 40.38% to 47.56% [3].

However, with the pyrolysis process, the fuel produced contains mixed hydrocarbon fractions with different chain lengths [4]. Fractional distillation is one method to separate gasoline fraction from this fuel. This separation process can be carried out continuously or batch-wise. The batch process is preferable with a small capacity unit or variable feedstock. The performance of the fractionation column can be estimated through mathematical modeling: rigorous and short cut model Various literature described a short cut model for batch multicomponent distillation in fractionation column [5-8]. In this research, the distillation of the pyrolysis results for gasoline fraction plastic waste with the help of co-reactants was carried out using a fractionated distillation column through experiment and simulation using a short cut model. The distillation process simulations were carried out to obtain the optimum conditions for the distillation process, which are expected to be used in the design of the distillation process.

2. Research Method

2.1. Experiment

The distillation sample obtained is the result of pyrolysis that has been carried out with a composition of 81-85% of the C8-C12 fraction; 4-12% fraction <<C7 and the remaining fraction >>C12. A simple distillation column was used with a diameter of 20 cm and a height of 75 cm with steel wool packing as shown in Fig. 1.

Fig. 1. Distillation batch

Distillation is carried out with a predetermined temperature and pressure of 453.15K and 1 bar according to the boiling point of the C8-C12 product by varying the reflux ratio (R). Then we collect results obtained and analyze RON, caloric value, and kinematic viscosities.

2.2. Modelling and Simulation

The modeling process used is batch distillation modeling with a shortcut method. In working on the gasoline fraction component, assumptions are made for the fraction close to it. The fraction below C7 is assumed to be Hexane with (A) notation, the fraction between C8-C12 is assumed to be Decana with (B) notation, and the fraction above C12 is assumed to be Pentadecane with (C) notation. So the calculation consists of 3 average components representing each fraction. The shortcut model is based on the assumption that batch distillation process operation can be structured by a series of short-duration continuous distillation operations. It employs a modified Fenske-Underwood-Gilliland (FUG) shortcut model of continuous distillation [6, 9]. Starting with an initial charge (B0, xb0) at time t=to and for a small interval of time t=t1-t0. The distillate rate can be calculated using [5]:

$$D = \frac{V}{1+R} \quad (1)$$

Where R is the reflux ratio that can define as R= L/D. At a small interval time $\Delta t = t1 - t0$, the quantity of distillate can be calculated as follows

$$Ha = D\Delta t \quad (2)$$

Massa balance becomes:

$$\mathrm{B0} = \mathrm{B1} + \mathrm{Ha} \quad (3)$$

Or:

$$\mathrm{B0}/\Delta t = \mathrm{B1}/\Delta t + \mathrm{Ha}/\Delta t \quad (4)$$

With F=$B_0/\Delta t$; B = $B_1/\Delta t$

$$\mathrm{F} = \mathrm{B} + \mathrm{D} \quad (5)$$

Component balance become

$$Fx_f^i = Bx_{b\,new}^i + Dx_D^i \qquad (6)$$

Garcia et al. [8] detailed the model by calculating Nmin and Rmin assuming the following Eduljee equation:

$$\frac{N-Nmin}{N+1} = 0,75\ [1 - \left[\frac{R-Rmin}{R+1}\right]^{0,5668}] \qquad (7)$$

Using the Underwood Equation class II assumption

$$\sum_{1=1}^{nc} \frac{\alpha_{1,r}(x_B^i)}{\alpha_{1,r} - \theta} = 1 - \mathrm{q} \qquad (8)$$

$$\sum_{1=1}^{c} \frac{\alpha_{1,r}(x_D^i)}{\alpha_{1,r} - \theta} = \mathrm{Rmin} + 1 \qquad (9)$$

Where the Underwood parameter, and i is the component notation in the mixture, and r is the reference component, which is the Heavy Key fraction. With the 9 Rmin equation validated after assuming equation 7. Then it can be calculated on the new distillate composition using the following equations:

$$\mathrm{x_B^i}\ \left[\frac{\mathrm{x_D^r}}{\mathrm{x_B^r}}\right] \alpha_{1,\mathrm{r}}^{\mathrm{Nmin}} = \mathrm{x_D^i} \qquad (10)$$

$$\left[\frac{\mathrm{x_B^r}}{\sum_{i=1}^{NC} \mathrm{x_B^r}\ \alpha_{1,\mathrm{r}}^{\mathrm{Nmin}}}\right] \alpha_{1,\mathrm{r}}^{\mathrm{Nmin}} = \mathrm{x_D^R} \qquad (11)$$

The relative volatility was estimated using the following vapor-liquid equilibrium equation for hydrocarbon.

$$K_i = \frac{P_{ci}}{P} \exp\left[5.37(1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right] \qquad (12)$$

Where the critical property data is obtained from the NIST data bank. This mathematical model is then carried out by simulation using the help of MS Excel 2016.

2.3. Analytical procedures

The analysis carried out after distillation is calculated kinematic viscosity, Research Octane Number, and Calorific Value, which is carried out at the ITS Energy and Environment Laboratory. Kinematic Viscosity Test Method using ASTM D-445-97, RON Using IKA/LEL-ITS/Octane-Cetane Analyzer and Calorific Value using Bomb Calorimeter. The viscosity value obtained can then be compared using the calculation equation proposed by Wakabayashi [10] with the equation 13:

$$\log v = 1.37\ (d\log M)^2 + 16.12\ (d\log M)\text{^}2 - 9.06 \qquad (13)$$

where d is specific gravity, M is molecular weight, and v is kinematic viscosity (mm2s-1)

3. Results and Discussions

3.1. Experimental Result

After the RON, Kinematic viscosity, and calorific value tests were carried out, it was found that the results of the distillation test shared the reflux ratio as follows:

Table 1 Characteristics of Distillation Results

Component	RON	Kinematic Viskocity (cst)	Caloric Value (cal/gr)
Feed	95.4	0.83	10577
Distillate (A) with RR =1	95.3	0.92	10677
Distillate(B) with RR =1	95.4	0.81	10588
Distillate A with RR =1,5	97.3	0.54	10426
Distillate B with RR = 1,5	97.2	0.83	10698
Distillate A with RR = 2	99.2	0.64	10421
Distillate B with RR = 2	101.4	0.74	10543
Bottom Product	103.1	3.05	10212

Sample A tents to light product C_7 or lower, and B is the main product C_8-C_{12}. With the addition of the reflux ratio, the RON also increases significantly. That proves that the reflux ratio causes the distillation of the desired product to be purer. Considering that the distillation carried out is a batch distillation, there may still be products mixed between light and heavy keys. The distillation process produces performance petroleum oil with RON 98 and caloric value 10,609,7 cal/gr. The distillation process can enhance the result of RON and caloric value due to the feed product. Compared to commercial petroleum oil, this result can be similar to petroleum oil from Pertamina with the brand name Pertamax Plus. This product has RON about 95 and a caloric value of 10,622 cal/gr. The other product is Shell with the brand name super extra - it has RON about 95 and caloric value 10,677 cal/gr.

3.2. Modelling and Simulation

Modeling and simulation of the batch distillation process of pyrolytic oil were done using the shortcut method [5, 6, 8, 9] with a pseudo component approach [11]. The simulation results show that the concentration of the desired product in distillate (product B) decrease with increasing distillation time at a constant reflux ratio of 1 (see Table 2).

Table 2 Simulation distillation using shortcut with R=2.5

Time	B1(Bottom)	Xb1 (bottom product)			Xd (instant distillation)			Xda (accumullate distillation)		
		A	B	C	A	B	C	A	B	C
0	3.85 (B_o = Feed)	0	0.22	0.78	0.124	0.866	0.010	-	-	-
0.5	3.837618	0	0.219	0.782	0.125	0.844	0.031	0.117	0.872	0.010
1	3.825236	0	0.217	0.784	0.125	0.833	0.042	0.114	0.854	0.032
1.5	3.812854	0	0.215	0.786	0.125	0.823	0.052	0.124	0.833	0.042
2	3.800472	0	0.213	0.789	0.125	0.813	0.062	0.124	0.823	0.053

In the results obtained, it is also known that the reflux ratio also causes the product of distillation B to increase at a high reflux ratio, which can be seen in Fig. 2 for the ratio between the reflux ratio and distillation product B with a distillation time of 0-2 hours. The higher the reflux ratio, the higher the yield of the product because the liquid-vapor contact is more effective, which causes the product to be purer.

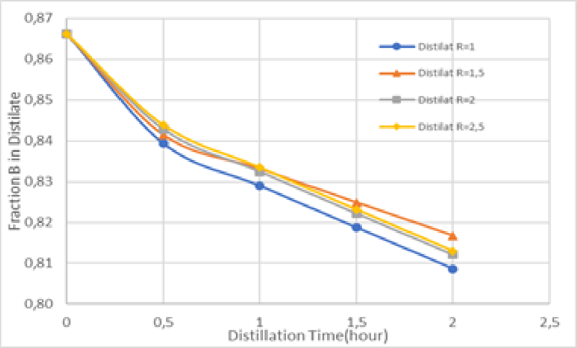

Fig. 2 Variation reflux ratio to distillation time and product fraction

The longer the distillation process, the higher the temperature reached for the dew pint on the distillate and the bubble point on the bottom. That is because the heat provided is constant, allowing for an increase in the temperature profile.

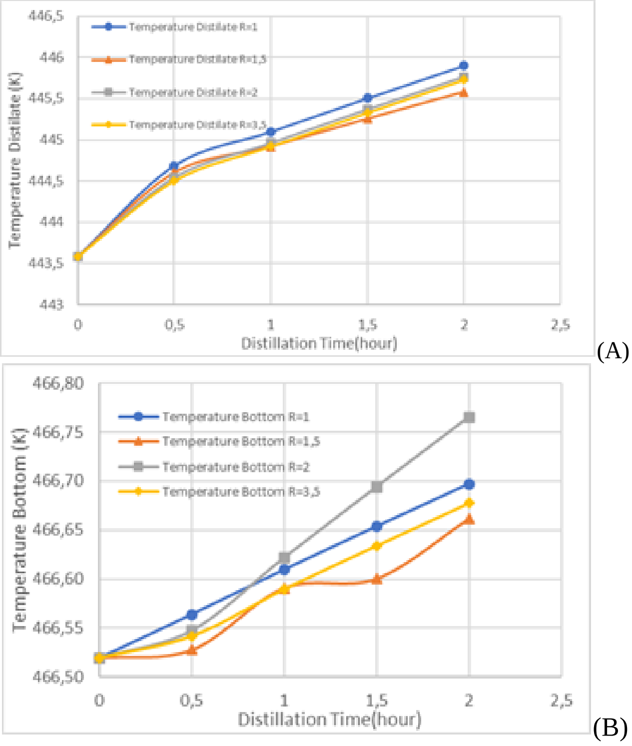

Fig. 3 Reflux ratio to retention time in (A) distillate product and (B) bottom Product

3.3. Comparation Model and Experimental

The modeling process was carried out to match the experimental results by knowing the equation using the formula to find kinematic viscosities with the following results.

Table 3 Kinematic viscosities after distillation with R=1

Time	Kinematic Viscosites (cst)
0	
0,5	9,267978
1	9,075663
1,5	8,891198
2	8,714168

There is a striking difference, which can be explained by the model used. The viscosity calculated from this equation has an average absolute deviation of 15.9% and is used to estimate the viscosity of crude oil [10]. The use of the shortcut method is a model that is quite practical so that the possibility of an error is quite high, which results in a significant difference. However, the higher the reflux ratio, the smaller the kinematic viscosities, and the longer the distillation time. The smaller the kinematic viscosities results.

4. Conclusion

The distillation process enhances the performance of petroleum oil with an average of RON 98 and a caloric value of 10,609,7 cal/gr. Modeling and simulation using excel of the distillation results of pyrolysis were carried out, it was found that the increase in the reflux ratio led to an increase in the purity of the distillation product and the effect of residence time caused the longer the process to run, the lower the distillation product. Therefore, the separation should not be done too long, which can cause the purity to decrease every time. The higher the reflux ratio, the smaller the kinematic viscosities get proven by experimental and modeling, but the value is a striking difference due to deviation from the model.

4.1. Credentials

The author would like to express gratitude to the Research and Community Service Foundation of Sepuluh Nopember Institute of Technology (DRPM-ITS) and for the financial support from the Deputy for Strengthening Research and Development of the Ministry of Research and Technology/National Agency for Research and Technology, with contract number 1177/PKS/ITS/2021.

References

[1] YULIANSYAH T. A., AGUS P., RAMADHAN A. A. and LAKSONO R. Pyrolysis of plastic waste to produce pyrolytic oil as an alternative fuel. *International Journal of Technology*, 2015, 6(7), 1076-1083. http://dx.doi.org/10.14716/ijtech.v6i7.1241

[2] THAHIR R., ALTWAY A., JULIASTUTI S. R., and SUSIANTO. Production of Liquid Fuel from Plastic waste using integrated pyrolysis method with refinery distillation bubble cap plate column. *Energy Report*, 2019, 5, 70-77. https://doi.org/10.1016/j.egyr.2018.11.004

[3] JUWONO H., TRIYONO T., SUTARNO S., WAHYUNI E. T., HARMAMI H., ULFIN I., and KURNIAWAN F. Production of Hydrocarbon (C7-C20) from Hydrocracking of Fatty Acid Methyl Esters on Pd/Al-MCM-41 Catalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*, 2017, 12(3), 337-342. https://doi.org/10.9767/bcrec.12.3.811.337-342

[4] ANUAR S., SHAFFERINA D., ABNISA F., WAN

DAUD W. M. A., and AROUA M. K. A review on pyrolysis of plastic wastes. *Energy Conversion and Management*, 2016, 115, 308-326. https://doi.org/10.1016/j.enconman.2016.02.037

[5] MUJTABA I. M. *Batch Distillation: Design and Operation*. Imperial College Press, London, 2004.

[6] SUNDARAM S., & EVAN L. B. Shortcut procedure for simulating batch distillation operations. *Industrial & Engineering Chemistry Research*, 1993, 32(3), 511-518. https://doi.org/10.1021/ie00015a014

[7] ZAMAR S. D., SALOMONE E., and IRIBARREN O. A. Shortcut method for multiple task batch distillations. *Industrial & Engineering Chemistry Research*, 1998, 37(12), 4801. http://dx.doi.org/10.1021/ie9800795

[8] GARCIA A. N., LORIA J. C. Z., MARIN A. R., and QUIROZ A. V. C. Simple multicomponent batch distillation procedure with a variable reflux policy. *Brazilian Journal of Chemical Engineering*, 2014, 31(2), 531-542. https://doi.org/10.1590/0104-6632.20140312s00001590

[9] DIWEKAR U. M., & MADHAVAN K. P. Multicomponent Batch Distillation Column Design. *Industrial and Engineering Chemistry Research*, 1991, 30, 713-721. https://doi.org/10.1021/ie00052a014

[10] WAKABAYASHI T. Viscosity Correlation with specific gravity and molecular weight of crude oil fraction. *Fuel*, 1997, 76(11), 1049-1056. https://doi.org/10.1016/S0016-2361(97)00090-2

[11] VAN WINKLE M. *Distillation*. McGraw Hill, New York, 1967.

参考文:

[1] YULIANSYAH T. A., AGUS P., RAMADHAN A. A. and LAKSONO R. 热解塑料废物以生产热解油作为替代燃料。国际科技杂志, 2015, 6(7), 1076-1083. http://dx.doi.org/10.14716/ijtech.v6i7.1241

[2] THAHIR R., ALTWAY A., JULIASTUTI S. R., 和 SUSIANTO. 使用炼油厂蒸馏泡罩板塔一体化热解法从塑料废料中生产液体燃料。能源报告, 2019, 5, 70-77. https://doi.org/10.1016/j.egyr.2018.11.004

[3] JUWONO H., TRIYONO T., SUTARNO S., WAHYUNI E. T., HARMAMI H., ULFIN I., 和 KURNIAWAN F. 在41号物质的钯/铝-美孚组合物催化剂上通过脂肪酸甲酯的加氢裂化生产烃 (碳7-碳20)。化学反应工程与催化通报, 2017, 12(3), 337-342. https://doi.org/10.9767/bcrec.12.3.811.337-342

[4] ANUAR S., SHAFFERINA D., ABNISA F., WAN DAUD W. M. A., 和 AROUA M. K. 废塑料热解研究综述。能量转换和管理, 2016, 115, 308-326. https://doi.org/10.1016/j.enconman.2016.02.037

[5] MUJTABA I. M. 批量蒸馏：设计和操作。伦敦帝国理工学院出版社, 2004.

[6] SUNDARAM S., & EVAN L. B. 模拟分批蒸馏操作的快捷程序。工业与工程化学研究, 1993, 32(3), 511-518. https://doi.org/10.1021/ie00015a014

[7] ZAMAR S. D., SALOMONE E., 和 IRIBARREN O. A. 多任务批量蒸馏的快捷方法。工业与工程化学研究, 1998, 37(12), 4801. http://dx.doi.org/10.1021/ie9800795

[8] GARCIA A. N., LORIA J. C. Z., MARIN A. R., 和 QUIROZ A. V. C. 具有可变回流策略的简单多组分间歇蒸馏程序。巴西化学工程杂志, 2014, 31(2), 531-542. https://doi.org/10.1590/0104-6632.20140312s00001590

[9] DIWEKAR U. M., 和 MADHAVAN K. P. 多组分间歇蒸馏塔设计。工业与工程化学研究, 1991, 30, 713-721. https://doi.org/10.1021/ie00052a014

[10] WAKABAYASHI T. 粘度与原油馏分比重和分子量的相关性。燃料, 1997, 76(11), 1049-1056. https://doi.org/10.1016/S0016-2361(97)00090-2

[11] VAN WINKLE M. 蒸馏。纽约麦格劳山, 1967.