

Optimization and Characterization Studies of Bio-Oil Production from *Jathropa curcas* L. Husk by Pyrolysis using Response Surface Methodology

*Salamiah Zakaria**, *Zaidi Ab Ghani*, *Mat Riduan Md Isa*, *Wahida Abdul Rahman*, *Noor Hafizah Uyup* and *Yuswanie Md Yusof*

Faculty of Applied Science, UiTM Perlis, 02600 Arau, Perlis
e-mail: salamiah882@perlis.uitm.edu.my

Abstract

*Biomass is one of the energy resources that can be exploited to replace fossil fuel. Combustion, pyrolysis and gasification are the main process to convert biomass into valuable fuel materials. In this study, *Jathropa curcas* L. husk was pyrolyzed to produce bio-oil. The effect of several parameters on the pyrolysis efficiency were tested to identify the optimal condition for the bio-oil production. The tested parameters include temperature, heating rate and gas flow rate. The experiments were conducted using vertical fixed-bed reactor. The response surface methodology (RSM) with a central composite design (CCD), were used for optimization the process parameters. From the study, the optimal conditions were obtained at pyrolysis temperature of 400°C, heating rate of 60°C/min and gas flow rate of 100ml/min with the amount of bio-oil produced was 28.9%. Furthermore, the bio-oil produced under optimum condition was characterized by using elemental analyser, bomb calorimeter, Fourier Transform Infra-red (FT-IR) spectroscopy and gas chromatography-mass spectroscopy (GC-MS).*

Keywords. *Jathropa curcas* L. husk, bio-oil, pyrolysis, Response Surface Methodology (RSM).

Introduction

Fossil fuel shortage and severe environmental problems have caused great attention on exploitation of clean renewable energies. Using biomass as a renewable energy source is a convenient way to produce energy without contributing to green house effect. Biomass can be converted into liquid by thermal, biological and physical methods. In thermal conversion the methods used are; combustion, gasification, liquefaction, pyrolysis and carbonization. Among them, pyrolysis is the most popular one. The pyrolysis process involves a cracking process on polymeric structure to convert the biomass into char and volatile matter. Numerous studies have been carried out to pyrolyse biomass for bio-oil (Onay et al., 2001; Acikgoz et al., 2007; Demiral and Sensoz, 2008; Putun et al., 2008).

Converting biomass into bio-oil makes it more efficient in many applications. Therefore, optimization by maximizing the desired product quality and quantity is an important issue to minimizing costs and environmental concerns. Nowadays *Jathropa curcas* L is planted for the production of oil as alternative fuel whereby *jathropa* oil has 16-18 carbon per molecule compare to diesel which has 8-10 (Openshaw, 2000). Hence, it will have higher viscosity and lower ignition quality

compare to diesel. The plants oil is usually transesterified to bio-diesel to reduce its viscosity and increase their cetane number so that it can be used in engines. Sricharoenchaikul et al. (2006) have done study on thermal decomposition on *Jathropa curcas* L. waste using TGA and fixed bed reactor. They found that the thermal decomposition of physic nut generally occurred over the temperature range of 250-450 °C. They also found that with increasing reactor temperature the char residue is decreased while gases product is increased.

Till now there are limited researches on pyrolysis of *Jathropa curcas* L. husk, hence an attempt has been made in this study to pyrolyze *Jathropa curcas* L. husk using fixed bed reactor. This paper studied the combined effect of the pyrolysis process parameters such as temperature, heating rate and gas flow rate, on the yield of bio-oil produced from *Jathropa curcas* L. husk based on central composite rotatable design in RSM. Also the bio-oil obtained under optimum conditions was characterized by using Bomb calorimeter, Fourier Transform Infra-red (FT-IR) spectroscopy and gas chromatography/mass spectrometry (GC/MS) techniques.

Materials and Methods

Materials and sample preparation

Jathropa curcas L. Husk samples used in this study were obtained from Universiti Teknologi MARA Arau campus farm. The husk sample was separated from the physical impurities and oven dried at 80°C to remove moisture. Then, they were grinded and screened to fractions with particles size of 200µm. The proximate analysis was performed on dried *Jatropha curcas L* husk by using Thermogravimetric Analyzer DTA/DSC TA Model SDT Q600 under

nitrogen gas atmosphere with heating condition follows the ASTM D2974. This analysis was to determine the weight fractions of moisture, volatiles, ash and fixed carbon (Table 1). Ultimate analysis was performed on husk sample to determine the elemental composition. The weight fraction of carbon, hydrogen, nitrogen and sulphur were determined using Elemental Analyzer Leco 932 model with helium gas as carrier by adopting the ASTM D2015, and the weight fraction of oxygen was calculated by the difference (Table 1). Calorific value of the husk sample was determined as 16.25 MJ/kg by using Bomb Calorimeter AC350.

Table 1: The Characteristic of *Jathropa curcas L.* Husk

| Proximate analysis (wt%) | | Elemental Composition (%) | |
|--------------------------|-------|---------------------------|------|
| Moisture | 9.55 | Carbon | 48.7 |
| Volatiles | 77.94 | Hydrogen | 5.7 |
| Fixed Carbon | 9.55 | Nitrogen | 1.1 |
| Ash | 2.96 | Sulphur | 0.2 |
| | | Oxygen* | 44.3 |

* By difference

Experimental Design

The parameters that affect to bio-oil production were studied using a standard of RSM design based on central composite design (CCD) (Aslan, 2008). In order to optimize the CCRD experimental design, a five-level two-factor CCRD was adopted in this study which required 20 set of experiments. These 20 experiments include 8 factorial points, 6 axial points and 5 central points. The number of test required for CCRD includes the standard 2^k factorial with its origin at the center, 2k points fixed axially at a distance, α , from the center to generate the quadratic terms, and replicate tests at the center; k is the number of the variables. The axial points are chosen such that they allow rotatability which ensures that the variance of the model prediction is constant at all points replicates of the test at the center are very important as they provide an independent estimate of the experimental error. For three variables, the recommended number of tests at the center is six. Hence the total number of tests required for the three independent variables (final temperature, heating rate and gas flow rate) is $2^3 + (2 \times 3) + 6 = 20$. Table 2 shows the experimental range and levels of the independent variables generated by the model. Once the desired ranges of values of the variables were defined, they were coded to lie at ± 1 for the factorial points, 0 for the center points and $\pm \alpha$ for the axial points. For pyrolysis of *Jathropa* husk, final temperature (A) (°C), heating rate (B) (°C/min) and

gas flow rate (C) (ml/min) were the independent variables selected for optimizing the liquid yield with the respective α value.

Pyrolysis Experiment

Pyrolysis experiments were performed in a stainless steel vertical fixed-bed reactor as shown in Figure 1. About 40g of sample with particles size of 200µm was placed in the furnace. The operating conditions for the furnace such as final temperature, heating rate and gas flow rate were set up by the RSM approach. The condensable products as liquid was collected and weighed. The product yield was calculated as follows:

$$\text{Yield (wt\%)} = \frac{\text{liquid product (g)}}{\text{Jathropa husk feed (g)}} \times 100\%$$

Analysis of bio-oil

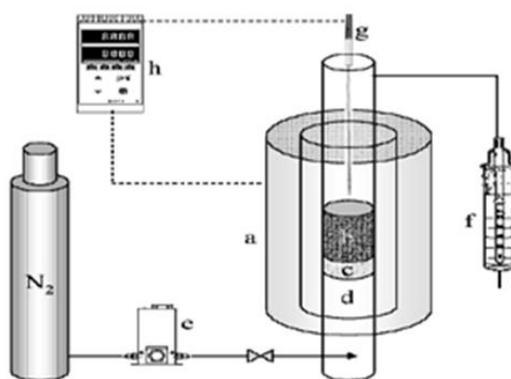
The bio-oil characterized in this study was obtained from optimum condition. Elemental Analyses were carried out on the bio-oil using CHNS/O elemental analyzer Leco 932. The calorific value of the bio-oil was determined by using a Bomb Calorimeter AC350. The gas chromatography-mass spectroscopy (GC-MS) was performed by using a Varians 4000 GC/MS/MS. The Fourier Transform Infra-red

(Model: Spectrum 400 (Perkin Elmer)) analysis was conducted to determine the functional group.

Table 2: Central composite design of independent variables for process optimization.

| Std | Coded | | | Actual | | |
|-----|--------|--------|--------|--------|-------|--------|
| | A | B | C | A | B | C |
| 1 | 0.000 | 0.000 | 0.000 | 500.00 | 45.00 | 150.00 |
| 2 | 1.000 | 1.000 | -1.000 | 600.00 | 60.00 | 100.00 |
| 3 | 0.000 | -1.682 | 0.000 | 500.00 | 19.77 | 150.00 |
| 4 | 0.000 | 0.000 | -1.682 | 500.00 | 45.00 | 65.91 |
| 5 | 0.000 | 0.000 | 0.000 | 500.00 | 45.00 | 150.00 |
| 6 | -1.682 | 0.000 | 0.000 | 331.82 | 45.00 | 150.00 |
| 7 | -1.000 | -1.000 | -1.000 | 400.00 | 30.00 | 100.00 |
| 8 | 1.000 | -1.000 | -1.000 | 600.00 | 30.00 | 100.00 |
| 9 | 0.000 | 1.682 | 0.000 | 500.00 | 70.23 | 150.00 |
| 10 | 1.682 | 0.000 | 0.000 | 668.18 | 45.00 | 150.00 |
| 11 | 0.000 | 0.000 | 0.000 | 500.00 | 45.00 | 150.00 |
| 12 | -1.000 | 1.000 | 1.000 | 400.00 | 60.00 | 200.00 |
| 13 | -1.000 | 1.000 | -1.000 | 400.00 | 60.00 | 100.00 |
| 14 | -1.000 | -1.000 | 1.000 | 400.00 | 30.00 | 200.00 |
| 15 | 0.000 | 0.000 | 0.000 | 500.00 | 45.00 | 150.00 |
| 16 | 1.000 | 1.000 | 1.000 | 600.00 | 60.00 | 200.00 |
| 17 | 0.000 | 0.000 | 0.000 | 500.00 | 45.00 | 150.00 |
| 18 | 1.000 | -1.000 | 1.000 | 600.00 | 30.00 | 200.00 |
| 19 | 0.000 | 0.000 | 0.000 | 500.00 | 45.00 | 150.00 |
| 20 | 0.000 | 0.000 | 1.682 | 500.00 | 45.00 | 234.09 |

A: final temperature (°C), B: heating rate (°C/min), and C: gas flow rate (ml/min)



Legend

- a) Tube furnace
- b) Sample
- c) Retainer
- d) Stainless steel tube
- e) Flow controller
- f) Condenser
- g) Thermocouple
- h) Controller

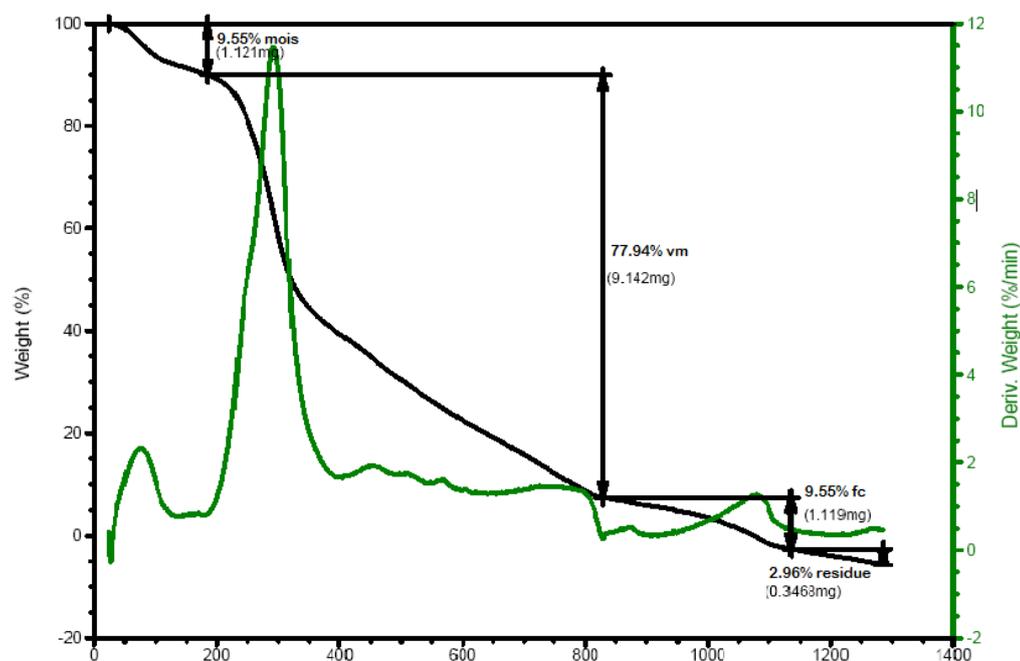
Figure 1: Pyrolysis reactor set up

Results and Discussion

Proximate analysis and pyrolysis behaviour of Jathropa curcas L. Husk

The proximate analysis for *Jathropa curcas L.* Husk is shown in figure 2. The content of moisture, volatile matter, fixed carbon and ash was found as 9.55%, 77.94%, 9.55% and 2.96% respectively. In this research, the TG analysis was used to view the thermal degradation curves of hemicelluloses, cellulose and lignin. It was observed that initial curved indicated moisture loss of up to 200°C. The *Jathropa curcas L.* Husk decomposed occurred at two stages during pyrolysis. The destructive reaction of cellulose and hemicellulose started between 250°C to 350°C and most of volatile materials decomposed within these temperatures. Therefore, the remaining residue above this temperature was considered as

char. In DSC curve, it can be seen that the fast decomposition occurred at 350°C which indicates the decomposition of cellulose compared to lignin. Generally the lignin is harder to decompose than the cellulose since part of lignin consists of benzene rings (Sharma et al, 2004). The study conducted by Isa et al. (2011) also proven that the standard cellulose material started to decompose at temperature ranging from 250 °C -390°C with T_{max} at about 370 °C. However, the standard lignin decomposed at a wider temperature ranging from 250 °C -500 °C. This information is very important in pyrolysis process to maximize the liquid contents since Li et al (2004) reported that the higher lignin composition of the apricot stone led to higher char as compared with that of legume straw. Hence in order to minimize char that caused by lignin degradation, the pyrolysis temperature should be set up correctly.

Figure 2: TGA/DSC curve for the *Jathropa curcas L.* husk sample.

Optimization

The significant factors screened in a fractional factorial design were investigated by using CCD for optimization. In these experiments, 20 runs were required to be investigated. The tabulated experiments and yield are given in Table 3. Process optimization was conducted to determine the optimal conditions of the process to obtain high percentage of bio-oil yield. The result from the software suggested the optimal conditions can be attained at pyrolysis

temperature of 400°C, heating rate of 60°C/min and gas flow rate of 100 ml/min and the bio-oil yield was 28.9%. The bio-oil yield could be improve by certain factor such as the increase of heating rate, suitable particle size, condensation temperature, lower ash content and lignin influences. Gani and Naruse (2007) suggested that the volatilization behaviour of biomass depends on its own component such as the cellulose and lignin content. By lowering ash content would result in a substantial increase in organic yield, while reaction water, char and gas yield are declined (Abdullah and Gerhauser, 2008).

Table 3: Pyrolysis results of *Jathropa curcas L.* husk at various temperature, heating rate and gas flow rate.

| Standard | Factor A: Temperature (°C) | Factor B : Heating Rate (°C/min) | Factor C : Gas Flow rate (mL/min) | Liquid yield (%) |
|----------|-------------------------------|--|---|------------------|
| 1 | 400 | 30 | 100 | 28.3 |
| 2 | 600 | 30 | 100 | 28.4 |
| 3 | 400 | 60 | 100 | 28.9 |
| 4 | 600 | 60 | 100 | 28.6 |
| 5 | 400 | 30 | 200 | 29.1 |
| 6 | 600 | 30 | 200 | 28.6 |
| 7 | 400 | 60 | 200 | 29.1 |
| 8 | 600 | 60 | 200 | 29.1 |
| 9 | 331.8 | 45 | 150 | 28.9 |
| 10 | 668.2 | 45 | 150 | 28.5 |
| 11 | 500 | 19.8 | 150 | 28.3 |
| 12 | 500 | 70.2 | 150 | 28.5 |
| 13 | 500 | 45 | 65.9 | 28.6 |
| 14 | 500 | 45 | 234.1 | 29 |
| 15 | 500 | 45 | 150 | 29 |
| 16 | 500 | 45 | 150 | 29 |
| 17 | 500 | 45 | 150 | 29 |
| 18 | 500 | 45 | 150 | 29 |
| 19 | 500 | 45 | 150 | 29 |
| 20 | 500 | 45 | 150 | 29 |

Effect of operating variables on the bio-oil products

Effect of final temperature and heating rate on the liquid yield

Figure 3 shows the relationship between effect of final temperature and heating rate on the liquid yield. It was observed that the liquid yield is decreasing with increasing temperature. Maximum yield was obtained at the temperature of 400°C while the lowest yield can be obtained at 600°C. The decreasing of product yield with respect to the increasing the temperature is might be due to the secondary reaction such as thermal cracking which will favor the formation of gas and low both oil and char yield (Ozbay et al., 2008)

Effect of final temperature and gas flow rate

Figure 4 shows the relationship between the final temperature and gas flow rate to the liquid yield. It can be observed that with increasing gas flow rate, the liquid yield also increasing. This is because high flow rate will shortens the residence time of pyrolysis vapors inside the reaction zone. Shorter residence time will prevent the secondary decomposition of the biomass from occurring that

will increase the gaseous product yield. The solid and liquid product yield would decrease if the secondary reaction occurs. Thus, by increasing the flow rate, the pyrolysis vapors will spend short time in the reaction zone. It will avoid the vapor from undergo secondary decomposition that will produce gaseous products (Ates et al., 2004)

Effect of heating rate and gas flow rate

The liquid yield is increasing with increasing heating rate (Figure 5). Highest liquid yield was obtained at heating rate of 60 °C/min. High heating rate provide high heat and mass transfer inside the biomass particles. This will result in higher conversion of the biomass to liquid and gaseous product. A study by Onay (2007) found that employing higher heating rate for all pyrolysis temperature breaks the heat and mass transfer limitations in the pyrolysis, resulting in the maximum liquid yield. It is also consistent with previous study conducted by Nazzal (2002). He found that the oil yield was increased with increasing heating rate from 2 to 10°C/min.

DESIGN-EXPERT Plot

Liquid %
 X = A: Temp
 Y = B: HR

Actual Factor
 C: FR = 150.00

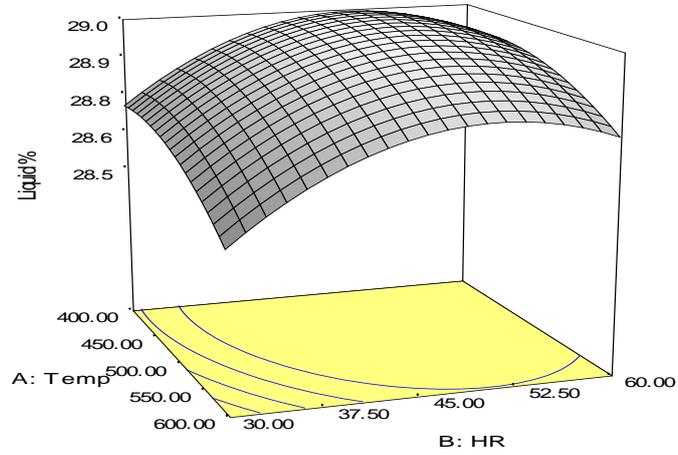


Figure 3: Relationship between effect of final temperature and heating rate on the liquid yield.

DESIGN-EXPERT Plot

Liquid %
 X = A: Temp
 Y = C: FR

Actual Factor
 B: HR = 45.00

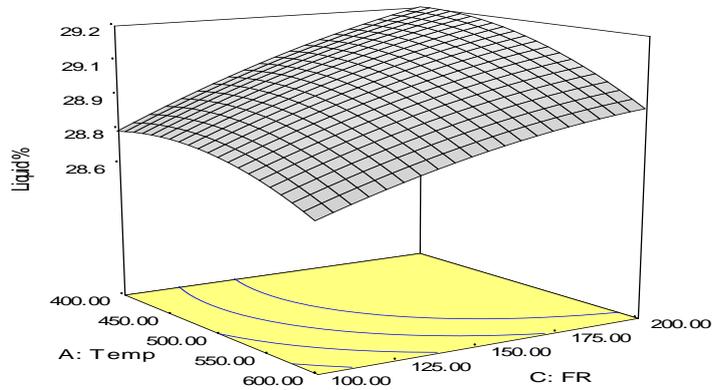


Figure 4: The relationship between the final temperature and gas flow rate to the liquid yield.

DESIGN-EXPERT Plot

Liquid %
X = B: HR
Y = C: FR

Actual Factor
A: Temp = 500.00

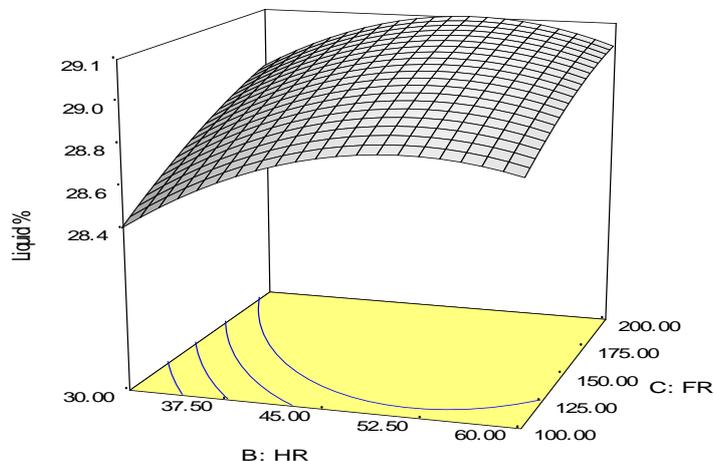


Figure 5: The relationship between the heating rate and gas flow to liquid yield.

Bio-oil Analyses

The ultimate analysis of the bio-oil and its calorific value was tabulated in Table 4. The percentage of C, N, H, S and O was found to be as 73.64%, 7.68%, 3.89%, 0.54%, and 14.35%, respectively. The calorific value of the bio-oil is 33.78 MJ/kg which is closed to the standard diesel fuel (44.8 MJ/kg) (Duan and Savage, 2011). The relatively high calorific value is due to the low oxygen content in the bio-oil. The H/C ratio that has been calculated is 0.62. This low H/C ratio indicates that the bio-oil is poor quality because it will produce high CO₂ emission during combustion. Bio-oil can be upgraded physically, chemically and catalytically (Bridgwater, 2012).

Several functional groups have been identified from the FT-IR spectra (Figure 6). A strong adsorption band at 1701 cm⁻¹ indicates the carbonyl group, C=O. Another strong band at 2925 cm⁻¹ indicates the C-H bonds for alkane while a medium absorption band at 3313 cm⁻¹ is for O-H bond for phenols. Lastly, a variable absorption band at 1506 cm⁻¹ indicates the C=C bond for the aromatic hydrocarbon.

GC-MS result provides valuable information on the distribution of hydrocarbon component in the oil. The qualitative GC-MS analyses on the oil produced at optimum condition indicate mainly the presence of cycloheptasiloxane, 1,2-benzenedicarboxylic acid, butylated hydroxytoluene and 1,3,5-trimethylbenzene (Figure 7).

Table 4: Ultimate analysis and calorific value of bio-oil.

| Element | Values |
|-----------------|-------------|
| C | 73.64% |
| N | 7.68% |
| H | 3.80% |
| S | 0.54% |
| O | 14.35% |
| H/C ratio | 0.62 |
| Calorific value | 33.78 MJ/kg |

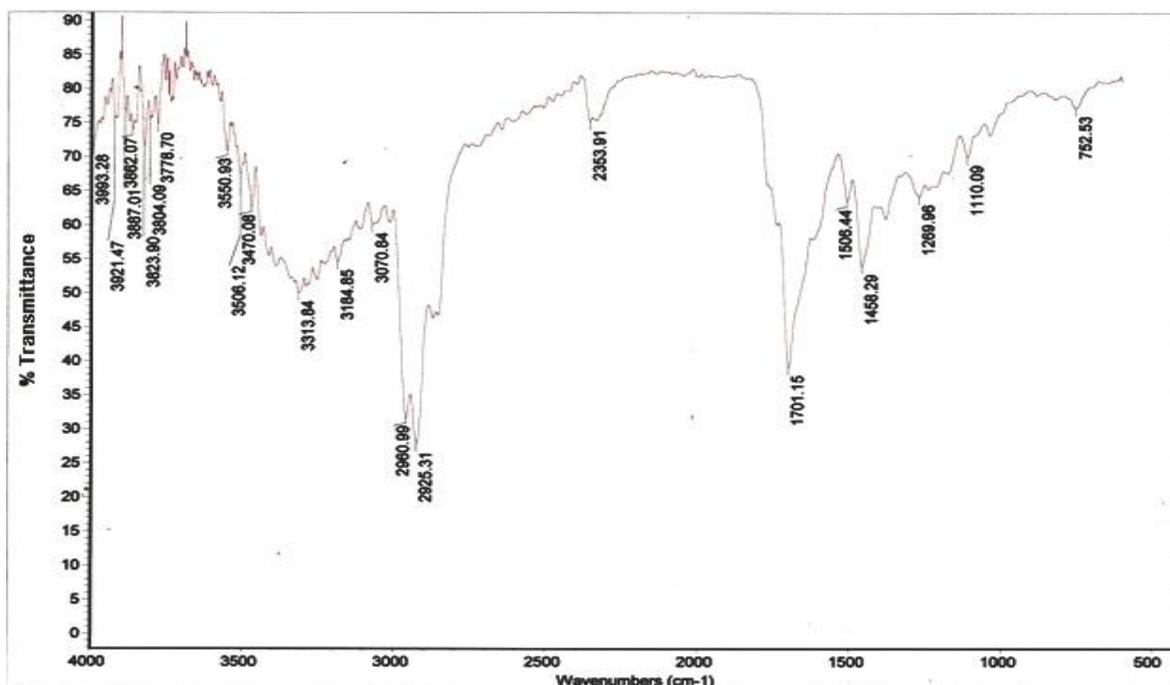


Figure 6: FT-IR spectra of the bio-oil

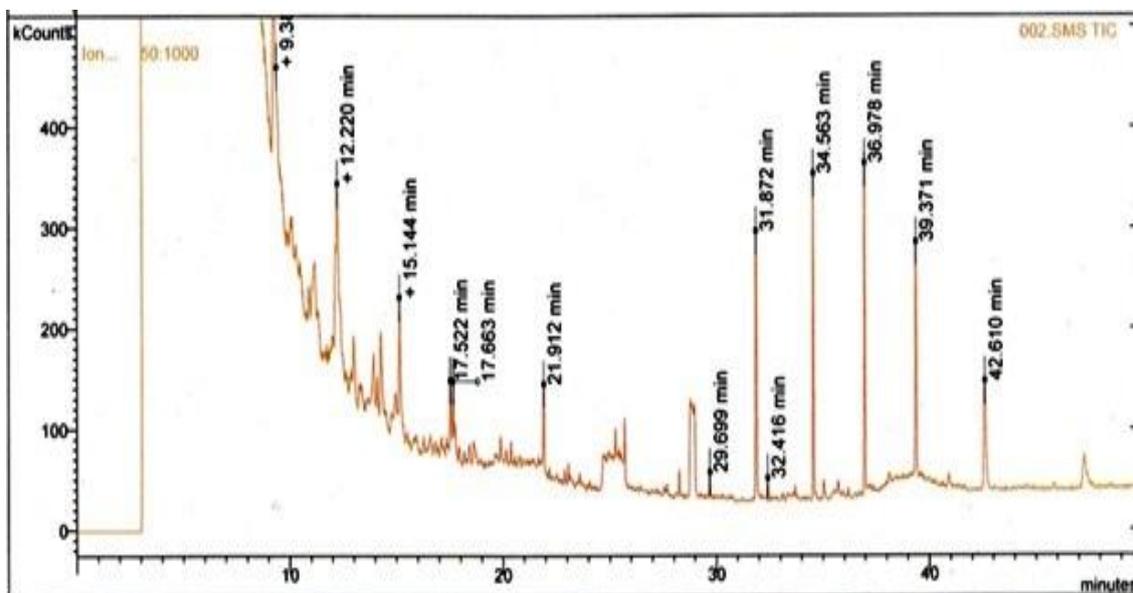


Figure 7: GC-MS spectrum of the bio-oil

Conclusion

The design-expert software was successfully employed to optimise the production of bio-oil via pyrolysis process using fixed-bed reactor. Factors such as pyrolysis temperature, heating rate and gas flow rate were tested which indicate significantly affected the production of bio-oil. These factors were utilised by RSM and it was found that the optimal condition were obtained at pyrolysis temperature of 400°C, heating rate of 60 °C /min and gas flow rate of 100ml/min.

The analyses of bio-oil produced at this optimal condition indicated the presence of

References

- Abdullah, N., and Gerhauser, H., (2008). Bio-oil derived from empty fruit bunches. *Fuel*, 87, 2606–2613.
- Acikgoz, C., Onay, O., and Kockar, O.M., (2004). Fast pyrolysis of linseed: product yields and compositions. *Journal of Analytical and Applied Pyrolysis*, 71, 417–429.
- Aslan, N., (2008). Application of response surface methodology and central composite rotatable design for modelling and optimization of a multi-gravity separator for chromite concentration. *Powder Technology*, 185, 80–86
- ASTM D2974, Annual Volume. 5.05 (ASTM) Philadelphia, PA, 1991.
- ASTM D2015, Vol. 5.05 (ASTM), Philadelphia, PA, 1994.
- Ates, F., Putun, A.E., and Putun, E., (2004). Fast pyrolysis of sesame stalk: yields and structural analysis of bio-oil. *Journal of Analytical and Applied Pyrolysis*, 71, 779–790
- Bridgwater, A.V., (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*, 38, 68–94
- Demiral, I. and Sensoz, S., (2008). The effects of different catalysts on the pyrolysis of industrial wastes (olive and hazelnut bagasse). *Bioresource Technology*, 99, 8002–8007.
- Duan, P., and Savage, P.E., (2011). Upgrading of crude algal bio-oil in supercritical water. *Bioresource Technology*, 102, 1899–1906
- Gani, A. and Naruse, I., (2007). Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass. *Renewable Energy*, 32, 649–661.
- Isa, K.M., Daud, S., Hamidina, N., Ismail, K., Saad, A.S., and Kasima, F.H., (2011). Thermogravimetric analysis and the optimisation of bio-oil yield from fixed-bed, *Crops and Products*, 33, 481–487
- Li, S., Xu, S., Liu, S., Yang, C., and Lu, Q., (2004). Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas. *Fuel Processing Technology*, 85, 1201–1211.
- Nazzal, J.M., (2002). Influence of heating rate on the pyrolysis of Jordan oil shale, *Journal of Analytical and Applied Pyrolysis*, 62, 225–238
- Onay, O., (2007). Influence of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed by pyrolysis, using a well swept fixed bed reactor. *Fuel Processing Technology*, 88, 523–531.
- Onay, O., Beis, S.H., and Kockar, O.M., (2001). Fast pyrolysis of rape seed in a well-swept fixed-bed reactor. *Journal of Analytical and Applied Pyrolysis*, 58–59, 995–1007.
- Openshaw, K. (2000). A review of *Jathropa curcas*: an oil plant of unfulfilled promise. *Biomass and Bioenergy*, 19, 1–15.
- Ozbay, N., Varol, E.A., Uzun, B. B., and Putun, A.E., (2008). Characterization of bio-oil obtained from fruit pulp pyrolysis. *Energy*, 33, 1233–1240
- Putun, E., Ates, F., and Putun, A.E., (2008). Catalytic pyrolysis of biomass in inert and steam. *Fuel*, 87, 815–824.
- Sharma, R.K., Wooten, J.B., Baliga, V.L., Lin, X., Chan, W.G., and Hajaligol, M.R., (2004). Characterization of chars from pyrolysis of lignin. *Fuel*, 83, 1469–1482

Acknowledgements

The authors are very thankful to the UiTM Perlis Farming Unit for kindly providing the biomass used.

Sricharoenchaiku, V., Marukatat, C., and Atong, D., (2006). Fuel production from physic nut (*Jatropha*

Curcas L.) waste by fixed-bed pyrolysis, The academic network of Energy of Thailand 3. 23-25 May, 2550 Baiyoke Sky. Bangkok.