การผลิตน้ำมันชีวภาพจากการไพโรไลซิสเปลือกเมล็ดกาแฟโดย Co/HZSM-5 และ Ni/HZSM-5 ด้วยเครื่องปฏิกรณ์แบบเบด-นิ่งและไมโครเวฟ

Bio-oil Production of Coffee Husk Pyrolysis by Co/HZSM-5 and Ni/HZSM-5 from Fixed-bed and Microwave Reactors

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ABSTRACT

The Coffee husk, known as a biomass waste, obtained from coffee industry is aimed at being value-added in bio-oil products. The bio-oil is an alternative energy source which is used to replace fossil fuels and reduce greenhouse gas emissions. This study highlights the production of bio-oil having high aromatic compounds from the coffee husk by pyrolysis process, which uses catalysts 2, 5, 10%wt. Co/HZSM-5 and 2, 5, 10%wt. Ni/HZSM-5 from Fixed-bed reactor (FBR) and Microwave reactors (MCR) at 450°C, 0.05 in catalyst/husk, and the size of 1.6-2.8 mm. This is carried out by comparing the yield of bio-oil and the aromatics in bio-oil investigated by GC/MS. The result shows that the yield of bio-oil accounts for 51.76 wt% as well as the yield of aromatics in bio-oil is 19.02 wt%, derived from 10%wt. Co/HZSM-5 with Microwave reactor. Therefore, the catalyst 10%wt. Co/HZSM-5 and the microwave reactor are chosen in order to perform the next experiment which aims to find the suitable condition of the bio-oil production. Then the experiment is conducted by modelling response surface method (RSM) with Box-Behnken design (BBD), which specifies 3 variables, namely the temperature in the range of 350-500°C, catalyst/husk ranging from 0.03 to 0.07, and the size of coffee husk ranging from 0.5 to 4 mm by encoding -1, 0, 1. It can be seen that the optimal condition for bio-oil production obtaining from the quadratic model was at 500°C, 0.07 in catalyst/husk, and the particle size of 2.8-4 mm. This leads to 49.46 wt% in the yield of bio-oil and 17.11 wt% for the yield of aromatic in bio-oil. Not only this, there are other invaluable elements in the chemical industry, such as furans, phenols, amines, and amides for agricultural, nutraceutical, biopharmaceutical, and in the food industry including antioxidant and antimicrobial agent.

Keywords: Bio-oil, Microwave pyrolysis, Co/HZSM-5, Coffee husk, Box-Behnken design

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บทคัดย่อ

งานวิจัยนี้ต้องการแสวงหาการเพิ่มคุณค่าให้กับชีวมวลเปลือกเมล็ดกาแฟและลดมลภาวะที่เกิดจากอุตสาหกรรมการผลิตกาแฟ น้ำมันชีวภาพนี้เป็นแหล่งพลังงานทดแทนเชื้อเพลิงฟอสซิลและลดก๊าซเรือนกระจก โดยการผลิตน้ำมันชีวภาพที่มีสารประกอบอะโรมาติกสูงจากเปลือกเมล็ดกาแฟด้วยกระบวนการไพโรไลซิส โดยใช้ตัวเร่งปฏิกิริยา 2, 5, 10%wt. Co/HZSM-5 และ 2, 5, 10%wt. Ni/HZSM-5 จากสองเครื่องปฏิกรณ์ คือแบบเบด-นิ่ง (FBR) และแบบไมโครเวฟ (MCR) ที่อุณหภูมิ 450 องศาเซลเซียส, สัดส่วนปริมาณตัวเร่งปฏิกิริยาต่อเปลือกเมล็ดกาแฟ (Catalyst/Husk) เท่ากับ 0.05, ขนาดเปลือกเมล็ดกาแฟ 1.6-2.8 มิลลิเมตร โดยทำการเปรียบเทียบร้อยละปริมาณผลได้ของน้ำมันชีวภาพ และร้อยละปริมาณของอะโรมาติกที่พบในน้ำมันชีวภาพจากการทดสอบด้วย GC/MS พบว่าร้อยละปริมาณผลได้ของน้ำมันชีวภาพเป็น 51.76 wt% ร้อยละปริมาณของอะโรมาติกในน้ำมันชีวภาพเป็น 19.02 %wt. ผลิตจากตัวเร่งปฏิกิริยา 10 %wt. Co/HZSM-5 ด้วยเครื่อง MCR ดังนั้นจึงเลือกตัวเร่งปฏิกิริยา 10%wt. Co/HZSM-5 และเครื่อง MCR ทำการทดลองเพื่อหาสภาวะที่เหมาะสมในการผลิตน้ำมันชีวภาพ โดยจำลองการทดลองด้วยวิธีพื้นผิวตอบสนอง (RSM) แบบบ็อกซ์-เบห์นเคน (Box-Behnken design, BBD) ซึ่งกำหนดตัวแปร 3 ชนิด ได้แก่ อุณหภูมิในช่วง 350-500 องศาเซลเซียส , Catalyst/Husk ในช่วง 0.03-0.07, ขนาดเปลือกเมล็ดกาแฟในช่วง 0.5-4 มิลลิเมตร ด้วยการเข้ารหัส (-1, 0, 1) ซึ่งรูปแบบสมการกำลังสอง (Quadratic model) พบสภาวะเหมาะสมสำหรับการผลิตน้ำมันชีวภาพที่ 500 องศาเซลเซียส, Catalyst/Husk 0.07, ขนาด 2.8-4 มิลลิเมตร พบร้อยละปริมาณผลได้ของน้ำมันชีวภาพ 49.46 wt% และร้อยละปริมาณของอะโรมาติกในน้ำมันชีวภาพ 17.11 wt% นอกจากนี้ยังมีองค์ประกอบอื่นๆ ที่มีคุณค่าในอุตสาหกรรมเคมี เช่น ฟูแรน ฟีนอล เอมีนและเอไมด์ สำหรับการเกษตร โภชนาการ ชีวเภสัชภัณฑ์ และอุตสาหกรรมอาหารโดยเป็นสารต้านอนุมูลอิสระหรือสารต้านจุลชีพ

คำสำคัญ: น้ำมันชีวภาพ ไมโครเวฟไพโรไลซิส Co/HZSM-5 เปลือกเมล็ดกาแฟ
การออกแบบบ็อกซ์ - เบห์นเคน

Introduction

Coffee is regarded as one of the beverages prevailing by millions of consumers in Thailand. Traditionally, coffee beans were made for a simply instant beverage; however, these decades the raw coffee beans are directly taken for processing the beverage which generates tasty odor and values to the luxurious beverage. Therefore, the demand of coffee beans in cafe industry experiences a noticeable rise, contributing to an increase in agricultural wastes such as coffee husks which are typically produced by the production process of coffee bean.

Moreover, according to the observation of International Coffee Organization (2019), not only did Thailand have an increasing rate in demand of coffee beverages, but the global cofee demand also witnessed a rising rate of 2.7% per year to 10.7% from 2015 to 2018. This means that coffee husks with respect to the coffee manufacturing process would increase, resulting in a growth in an agricultural waste disposal.

Sime *et al*. (2017) report that 2 kg of coffee beans can generate the 1 kg of its husk, considered to be the biomass waste . In Thailand, the coffee beans is generally produced around 36,000 tons/year, therefore the biomass waste would be generated about 18,000 tons/year. Regarding the global coffee production, the coffee bean is produced approximately 9.6 million tons/year, leading to 4.8 million tons/year of coffee husk. As a result, the purpose of this research is to utilize the value-added coffee husks instead of disposal of fuel waste by a typical combustion, affecting the serious environmental issues.

In order to reduce the negative impacts on the environment due to the elimination of coffee husk waste, several researchers have attempted to convert the biomass into valuable products such as ethanol (Sime *et al*., 2017) and char fuel (Merete *et al*., 2014). According to the study conducted by Harsono, Dila,& Mel (2019), the property and efficiency of coffee husk are analyzed by estimating the amount of moisture and ash production. It appears that coffee husks can reasonably be converted into bio-char pellet. Therefore, this study aims to utilize a value-added agricultural waste from coffee husk in Thailand, contributing to bio-oil employed by pyrolysis, where this utilization is considered to be the additional incomes of agriculturers.

Pyrolysis is a thermal decomposition process, converting biomass into valuable fuel products in the absence of oxygen under the temperature ranging from 200 to 1000°C. The obtaing products are bio-oil, bio-char and bio-gas. The proportions of products are different corresponding to various pyrolysis modes. Fast pyrolysis has hot vapor residence times which is less than 1 s. Recently, the bio-oil has gained interest due to the fact that liquids is convenient to store and transport, which can be used as an energy, chemicals, and a carrier of energy (Bridgwater, 2012). There are a number of factors affecting these products, including types of biomass, operating temperature, flow rate of nitrogen, and an amount of catalyst employing throughout the process (Zaman *et al*., 2017). Compared the conduction and convection of Fixed-bed (FBR) with Microwave reactor (MCR), the microwave heating is internal heat transfer and capable of direct heating to molecules of biomass through electromagnetic field. This means that the large biomass can be heated by the microwave without proceeding the pretreatment process of the raw material, which can reduce the expenditures and time consumption in this process (Li *et al*., 2017).

The bio-oil obtained by pyrolysis is found to be inconsistent with the requirements. This is because it is highly acidic containing low aromatic compounds and high oxygenated compounds, resulting in lower yield of bio-oil. This would lead to the improvement in the quality of bio-oil by using a catalyst to assist in the pyrolysis process (Rahman, Liu, & Cai, 2018), which would cause cracking, Decarbony-lation, Decarboxylation, Hydrocracking, Hydro-deoxygenation, Hydrogenation. Transition metals are added so as to make the catalyst more efficient. The cobalt and nickel are used for triggering the hydrodeoxygenation (HDO) reactions which can be easily removed oxygen compounds. Vichaphund *et al.* (2015) upgrade Co/HZSM-5 and Ni/HZSM-5 with the aim of producing aromatic compounds from catalytic fast pyrolysis of Jatropha residues by wet impregnation. It is apparent that not only does HZSM-5 promote higher aromatic compounds, but Metal/HZSM-5 would also result in a reduction in oxygen and nitrogen composition.

Regarding the study performed by Xie *et al.* (2014), microwave-assisted catalytic pyrolysis from sewage sludge is applied to produce bio-oil with HZSM-5. The result shows the yield of bio-oil and the lowest proportions of oxygen- and nitrogen-containing compounds on account of applying HZSM-5 and effectively heating by the microwave. Li *et al.* (2017) apply response surface methodology in which the Box-Behnken design is used for investigating the optimum conditions for microwave-assisted pyrolysis of cotton stalk with 3 variables operation which is a microwave power (1700-1900 W), reaction time (15-25 min), and reaction temperature (500-600°C). The result shows the highest bio-oil yield of 32.47 wt% at 1800 W, 24 min, and 550°C. Abas, Ani, & Zakaria (2018) applied microwave-assisted to produce pyrolysis liquid oil from oil palm fiber by using response surface methodology by means of central composite design experiment, which 3 variables are defined, namely holding time (15-30 min), activated carbon (50-70 g), and final temperature (400-600°C). It was found to be 41.7 wt% of bio-oil and 25.28 wt% of phenolic compounds in bio-oil.

Therefore, the purpose of this study is to seek value-added coffee husks to the farmer and reduce the detrimental effects to environments by converting the husks waste into bio-oil. The study focuses on high-value aromatic compound in bio-oil such as furans, phenols, amines, and amides which are typically widespread in agriculture, food nutraceutical, biopharmaceuticals, and the food industry regarding as an antioxidant and antimicrobial agent. The study is aimed at investigating the effects of operating temperature, the ratio of catalyst to the amount of coffee husk (Catalyst/Husk), and the appropriate size of coffee husk with respect to the bio-oil yield. The reaction is carried out by fixed-bed and microwave reactors, with the catalyst of Co/HZSM-5 and Ni/HZSM-5. The bio-oil yield is then determined and the qualitative research of bio-oil is analyzed by employing gas chromatography-mass spectrometer (GC-MS).

Materials and Methods

2.1 Coffee husk

The Robusta coffee husk can be found in a farm in Chumphon, Thailand, where the raw material is harvested in December 2018. Proximate and Elemental analysis are analyzed by Thermogravimetric analyzer (Perkin Elmer - TGA8000) and the CHNS/O Analyzer, FlashEA 2000 in accordance with ASTM standards from the Scientific and Testing Center of Prince of Songkla University. In the next stage of the process, the the coffee husk is groung and cut before being separated the size by mesh sieve no. 5, 8,12 and 35, which leads to the coffee husk size of 0.5-1.6, 1.6-2.8, 2.8-4 mm. After checking the moisture content which is at 11.4% by weight, the coffee husk is dried at 105°C for 24 hours in order that the moisture content was less than 10% by weight (Ji *et al.*, 2015; Ly *et al.*, 2019), leading to an increase in the efficiency of pyrolysis.

2.2 Catalyst synthesis

Reagents being used in the preparation of catalysts are associated with the dry impregnation and the catalytic reaction: NH_4-ZSM-5 zeolite with a ratio SiO_2/Al_2O_3 of 30 and a surface area of 425 m^2/g, obtaining from Zeolyst International (Conshohocken, PA, USA), Nickel Nitrate Hexahydrate: $Ni(NO_3)_2.6H_2O$, purity 99.0% , M.W. 290.8 from LOBAChemie company, Cobalt(II) Nitrate Hexahydrate: $Co(NO_3)_2.6H_2O$, purity 98.0%, M.W. 291.03 from SIGMA-ALDRICH. To begin, NH_4-ZSM-5 zeolite is heated by Calcination at 550°C, 6 hours for HZSM-5 (Kostyniuk, Key, & Mdleleni, 2019). Cobalt and Nickel 2,5,10%wt. metal/HZSM-5 are then dissolved in water in accordance with ratio HZSM-5/water: 1/1.532 g. In the next step, the Cobalt solution and Nickel solution are mixed with HZSM-5 support before putting into the oven at 105°C, 24 hours. For 2, 5, 10%wt.Co/HZSM-5, the calcination process is taken at 500°C for 6 hours, while the process for 2, 5, 10%wt.Ni/HZSM-5 is calcined at 600°C, 5 hours (Vichaphund *et al*., 2015). Finally, the amount of metal in catalysts is analyzed by Perkin Elmer, Optima 4300DV, ICP-OES under the testing condition at 25°C, argon gas pressure of 80 psi, nitrogen gas pressure of 30 psi, peristaltic pump flow at 1.5 ml/min, auxiliary flow rate at 1 L/min, nebulizer flow rate at 1 L/min, and plasma flow rate at 15 L/min.

2.3 Experimental setup and procedure

2.3.1 Fixed-Bed Reactor (FBR)

Pyrolysis operating system with thermal conductivity is shown in Figure 1. The fixed-bed pyrolysis equipment set is as follows: (1) Nitrogen gas tank, (2) furnace, (3) coffee husk and catalyst being packaged in rector with 30 mm inner diameter and 350 mm in length, (4) Pyrolysis product's tube, (5) Bio-oil collectors, (6) Condenser. Firstly, 13 g of the coffee husk is prepared, with the value of Cat./Husk to be 0.05. After adjusting the rate of nitrogen flow at 60 ml/min, the temperature is set to 450°C and then it should be waiting until reaching at the desired temperature. Following this, the timer can be started and set for 90 minutes. At the end of the setting time, the closed button for the reactor is pressed, but the nitrogen gas is still be opened so as to expel the remaining gas from the reactor in the system for 10 minutes. Ice is continuously added to the condensing unit. Each set of experiments is repeated three times and the average values are reported (Saad, Ratanawilai, & Tongurai, 2015).

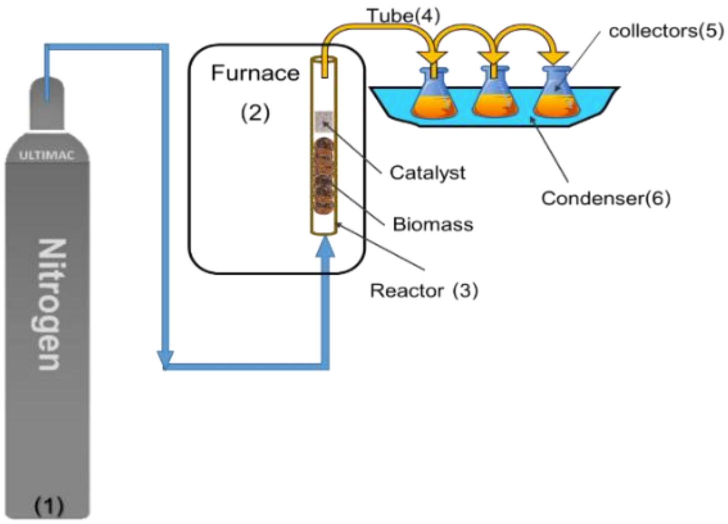

Figure 1 Fixed-bed Reactor.

2.3.2 Microwave Reactor (MCR)

To begin, the coffee husk in 50 g , silicon carbide (SiC) in 300 g are prepared to absorb microwave radiation and rapidly rising accelerate the heat by applying the catalyst with the value Cat./Husk to be 0.05. The tools and equipment are shown in the Figure 2 by setting the power to 1000 W, the frequency of 2450 MHz and turning on the pressure pump (Xie *et al*., 2014). Next, the microwave is started using to heat for 90 seconds and rest for another 45 seconds. During the rest, the microwave is measured using an infrared thermometer. When the specified temperature of 450°C, the timer starts for 90 minutes before stopping the microwave. After 2-3 minutes, pressure pump is then closed (Liu *et al.*, 2016). During pyrolysis process, ice should be continuously added to the condensing unit since the glass stopper could be bounced off, causing a harm due to the gas pressure. The final step is done by taking liquid products in glass bottles and in the section of biochar to weigh, record and calculate in order to identify the yield of each product according to the equation(Dai *et al.*, 2019). Each experiment is repeated three times to ensure data reliability and accuracy.

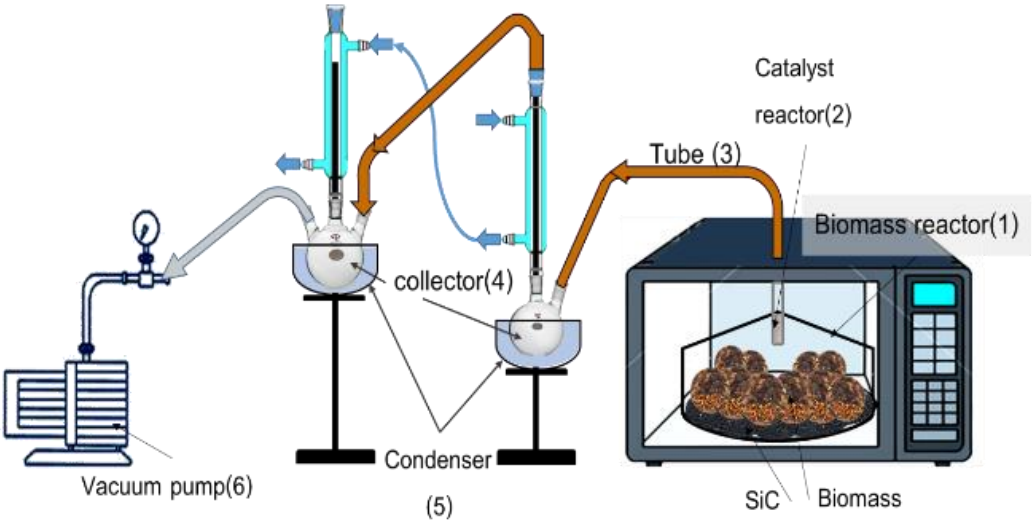

Figure 2 Microwave Reactor

2.4 Product analysis

The pyrolysis product consists of 3 state substances which are biochar, bio-oil, and biogas. The percent yield (wt%) in each state of substance is calculated by using mass balance, as shown in the following equations:

$$\text{Yield of bio-oil (wt\%)} = \frac{\text{Weight of bio}-\text{oil (g)}}{\text{Weight of biomass used (g)}} \times 100 \qquad (1)$$

$$\text{Yield of biochar (wt\%)} = \frac{\text{weight of bio}-\text{char (g)}}{Weight\ of\ biomass\ used\ (g)} \times 100 \qquad (2)$$

Yield of biogas (wt%) = 100 - Yield of bio-oil (wt%) - Yield of biochar (wt%) (3)

Gas Chromatograph(7890;GC)-Mass Spectrometer (7000D; MSD), Agilent, USA is a device which is used for analyzing the composition of bio-oil with the VF-WAXms column for 30 m in length, 0.25 mm inner diameter, film thickness of 0.25 µm, fused silica capillary tubing, 7-inch cage. Injector is fed at a temperature of 250°C, a pressure of 8.23 psi, with a carrier gas flow rate of 3 ml/minute, a split ratio of 20:1. After having the oven temperature at 60°C for 2 minutes, the heat is then increased to 250°C at the rate of heating for 5°C/minute and this temperature is maintained for 10 minutes. The results shows the percentage peak area of the bio-oil composition (% peak area), which is determined by comparing with the mass spectra in the National Institute of Standards and Technology (NIST). The perform function is then groupped and the yield of aromatic (wt%) is calculated as illustrated in Eq.4 (Mo *et al.*, 2014).

$$\text{Yield of Aromatic (wt\%)} = \text{Yield of bio-oil (wt\%)} \times (\%\ \text{peak area}) \div 100 \qquad (4)$$

2.5 Box-Behnken design (BBD)

Based on the results of the experiments on the types of catalysts and reactors, 10% wt. Co / HZSM-5 and MCR are chosen to test and determine the optimum conditions for bio-oil production. The Box-Behnken (BBD) design is used in RSM as the number of trials can be reduced, leading to more suitable results. The quadratic regression equation is expressed in Eq (5)

$$\mathbf{Y} = \boldsymbol{\beta_0} + \sum_{i=1}^{k} \boldsymbol{\beta}_{\mathrm{i}} \boldsymbol{x_i} + \sum_{i=1}^{k} \boldsymbol{\beta}_{\mathrm{ii}} \boldsymbol{x_i^2} + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \boldsymbol{\beta_{ij}}\, \boldsymbol{x_i x_j} + \boldsymbol{\varepsilon} \qquad (5)$$

When Y is the response or the yield of bio-oil. β_0 is a constant coefficient, while β_i, β_{ii}, β_{ij} are linear coefficient, quadratic coefficient and interaction effects coefficient respectively. X_i and X_j are independent variables, which are deternined by using codes instead. As shown in Table 1 (Abas, Ani, & Zakaria, 2018; Ismail *et al.*, 2013; Li *et al.*, 2017; Mo *et al.*, 2014), the three main parameters affecting the pyrolysis process are A: Temperature (Degree Celsius), B: Cat./Husk, and C: coffee husk size (Size, mm). All parameters were identified into three levels, which are -1, 0, and 1. There are 15 experiments, where 12 trials are at various points and 3 trials are at the midpoint in order to evaluate the experimental error and verify the suitability of the proposed model. The method of the experiment based on Section 2.3.2 Microwave Reactor (MCR) is shown in Table 4. The results are then evaluated using the Analysis of Variance (ANOVA).

Table 1 BBD experiments

A: Temperature, Celsius	B: Cat./Husk	C: Size, mm	Code Level
350	0.03	0.5-1.6	-1
425	0.05	1.6-2.8	0
500	0.07	2.8-4	1

Results and Discussion

3.1 Coffee husk

According to Figure 3, the initial stage where the temperature is less than 197°C is the reduction in moisture and volatile matter with small molecular weight. The second phase is between 197-700°C, where the decomposition of volatile matter or lignocellulose transforms into bio-oil. Hemicellulose decomposes in the temperature ranging from 196 to 275°C. The decomposing temperature of cellulose varies from 275 to 427°C, while lignin decomposes in the range of 196-700°C. In the final stage where the temperature is over 700°C is the decomposition of inorganic (Garba *et al.*, 2018; Ji *et al.*, 2015). In order to achieve the purpose of bio-oil production in this research, the experiment of pyrolysis is performed in the range of 350-500°C.

Table 2 indicates the amount of moisture of 11.4 wt%, which should not be more than 10 wt% (Capunitan & Capareda, 2012). The coffee husk is dried at 100°C for 24 hours to make the moisture contents to be suitable for pyrolysis. Ash content, Fixed Carbon, and Volatile matter are at 3.3 wt%, 14.4 wt%, and 70.9 wt% respectively. The Composition of coffee husk elements is as follows: Carbon (C) at 44.53 wt%, Hydrogen (H) at 5.97 wt% , Oxygen (O) at 39.25 wt%, Nitrogen (N) at 1.34% wt, Sulfur (S) at 0.074% wt. The results of this research is then compared with the results from Capunitan & Capareda (2012), since the results related to the proximate analysis and elemental analysis are similar, and there was no research on the coffee husk being used for pyrolysis, which bio-oil yield of Capunitan & Capareda (2012) is at 31.4 wt%. Therefore, it is expected that the yield of bio-oil from this research will be approximately the same. The amount of element affecting the composition of bio-oil will be produced from the pyrolysis process. According to the research conducted by Capunitan & Capareda (2012), the oxygen-aromatic is mostly found in bio-oil such as phenolic, which can be applicable for this research. Not only this, the HZSM-5 catalyst is used in order to enhance the quality of bio-oil in pyrolysis (Garba *et al.*, 2018).

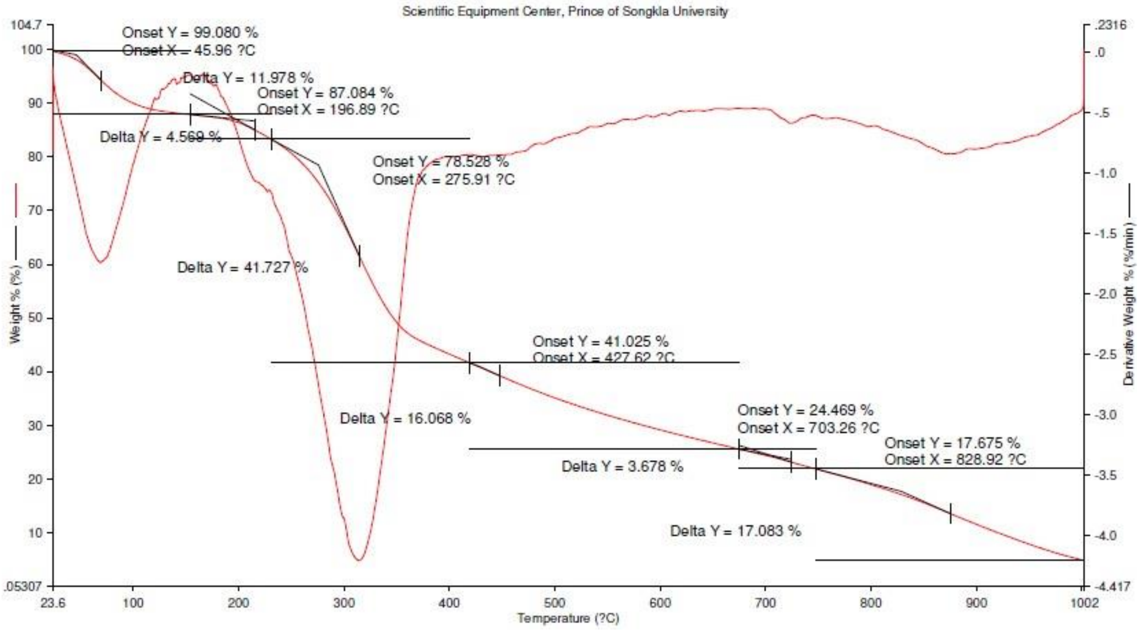

Figure 3 TG and DTG of the coffee husk

Table 2 The coffee husk properties

Feed biomass	Test Results ± SD (wt%)								
	Proximate analysis $^{\text{Dry basis}}$				Elemental analysis $^{\text{Dry ash-free}}$				
	Moisture	**Ash**	**Fixed Carbon**	**Volatile matter**	**C**	**H**	**O**	**N**	**S**
Coffee husk	11.407	3.336	14.367	70.890	44.53 ± 0.10	5.97 ± 0.21	39.25 ± 0.33	1.34 ± 0.03	0.074 ± 0.001
Corn stover	6.18	6.62	14.7	78.7	44.3	6.28	41.8	0.8	0.23

3.2 Catalyst characteristics

In relation to the catalytic test by ICP-OES which metal content is evaluated, the result as shown in Figure 4 expresses that for the catalyst 2, 5, 10%wt. Co/HZSM-5, the Cobalt II content is found to be 1.09 wt%, 2.33 wt%, and 7.45 wt% respectively, whiile the content of nickel by applying the catalyst 2, 5, 10%wt. Ni/HZSM-5 is equal to 1.65 wt%, 4.16 wt%, and 8.19 wt% respectively.

Since the behavior of cobalt (Co) and nickel (Ni) metals loaded on HZSM-5 supports is relatively different (Kostyniuk, Key, & Mdleleni, 2019). There is also the difference between these crystal structures, affecting the distribution on the HZSM-5 support including the process of preparation for the catalyst. This would result in the loss of metal content as the tested metal content does not match the theoretical values (Vichaphund *et al*., 2015

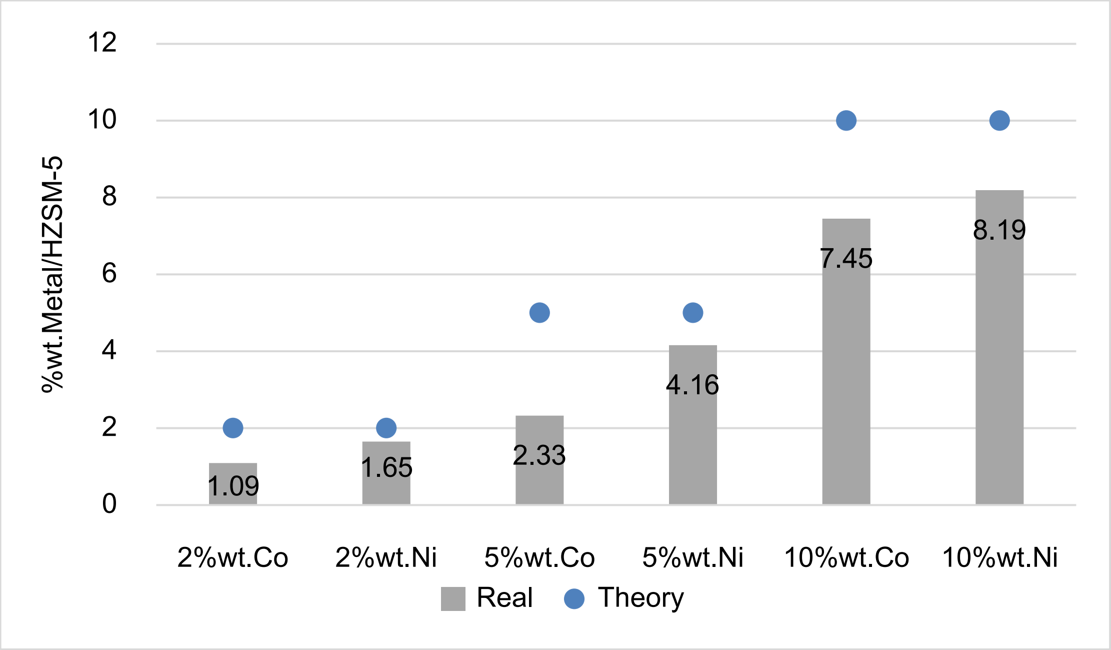

Figure 4 The amount of metal/HZSM-5 from ICP-OES

3.3 Comparative results of product yield of bio-oil from the FBR and the MCR

Figure 5 shows the comparison of the yield of bio-oil obtaining from the FBR and MCR with the same condition at 450°C, 0.05 in Cat./Husk, and the size of coffee husk of 1.6-2.8 mm (code level = 0, 0, 0) for 90 min, with the exception of the case of no catalyst, which means that the pyrolysis operation is done without the use of catalysts. In this case, the yield of bio-oil is 36.87 wt% and 44.75 wt% from FBR and MCR respectively. In the case of using Co/HZSM-5, the metal content ranges from 2 wt% to 10 wt% in the case of the FBR and the MCR, resulting in an increase in the yield of bio-oil. This means that regarding the case of the FBR, the yield of bio-oil rises from 34 wt% to 40 wt%, while there is a growth in bio-oil yield in the case of MCR from 40 wt% to 52 wt%. For the case of Ni/HZSM-5, where the metal content increases from 5 wt% to 10 wt% results in the rise in the yield of bio-oil ranging from 32 to 37 wt% from the FBR and 45 to 74 wt% from the MCR. However, the yield of bio-oil using a catalyst 2%wt. Ni/HZSM-5 appears to be different from other types of catalysts with nickel-based catalysts. The yield of bio-oil is 38 wt% and 49 wt% from the FBR and the MCR respectively, which is higher than the case of 5%wt. Ni/HZSM-5 and 10%wt. Ni/HZSM-5. This is because the type of catalyst and the amount of metal loaded on HZSM-5 have different reactions to volatile substances from pyrolysis, resulting in the yield of bio-oil.

As shown from the experiment, the yield of bio-oil obtaining from the MCR is higher than that of FBR due to the heating method of the reactor. The heating approach of the MCR is the radiation in order to vibrate the coffee husk molecules, resulting in more efficient than the FBR (Nhuchhen *et al.*, 2018), in constrast to the heating method by the FBR, which heats the coffee husk by conduction and convection. Therefore, the MCR is selected so as to consider and perform the next step of the experiment. The type of catalyst also affects the yield of the bio-oil.

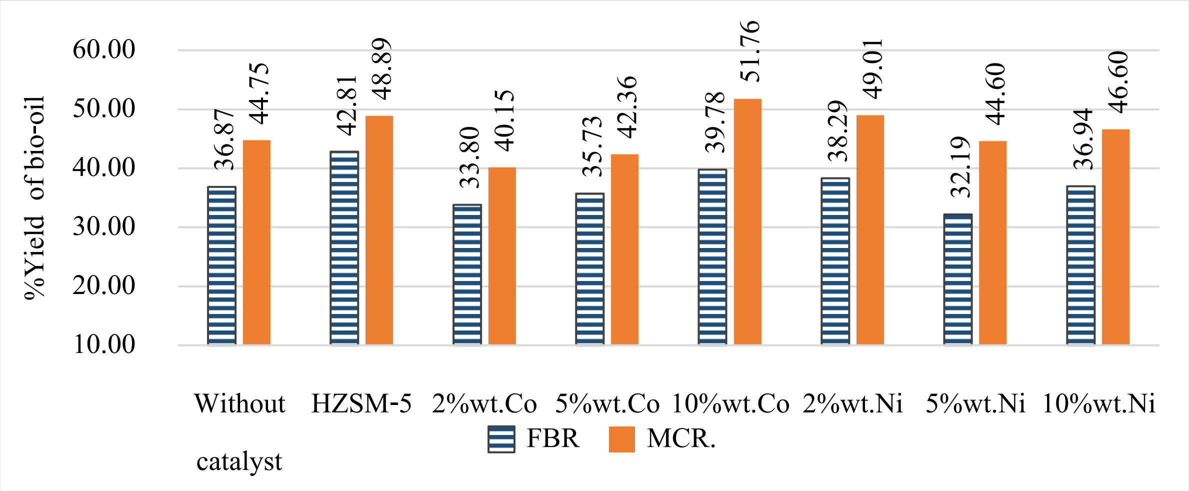

Figure 5 The yields of bio-oil from the FBR and the MCR at 450°C, Cat./Husk 0.05, 1.6-2.8 mm, 90 min.

3.4 Results of the yields of aromatic in bio-oil

Table 3 shows the functional grouping of aromatic constituents founded in the bio-oils from microwave reactors of each catalyst at 450°C, catalyst/husk content of 0.05, size of 1.6 mm. In GC/MS analysis, aromatic constituents from functional groupings in bio-oil are expressed as furans, phenyl, amine/amide, alkane/ alkene/alkyne, alcohol/ether, ketone/aldehyde, and acid/ester. Since there are definite benefits for aromatic compounds in performing good volumetric energy, aromatic compounds can also be used as coatings and adhesives to protect equipment such as seal-swells, O-rings, self-sealing bladders, adhesives in jet engine systems. In addition to this, furans are typically costly with considering value-added chemicals and phenols are commonly used in the cosmetic and pharmaceutical industries (Vichaphund *et al.*, 2015).

For performing pyrolysis without catalyst, the amount of aromatic (% peak area) is 31.19 wt%, while the amount of aromatic using the HZSM-5 catalyst is increased to 38.05 wt%. However, the amount of aromatic is around 33.94, 35.53, 36.74 wt% when the catalyst type is changed to 2, 5, 10%wt. Co/HZSM-5 respectively. In the case of 2, 5, and 10% wt. Ni/HZSM-5, the content of aromatic is about 38.46, 36.77, and 38.44 wt% respectively. It can be seen that adding the amount of cobalt and nickel would affect an increase in the presence of aromatic components.

Compared without catalyst to using HZSM-5 catalyst, the aromatic constituents are observed to be higher owing to the weak acidic action of Crystalline aluminosilicates in combination with the Mesoporous nature. The cobalt and nickel are added, resulting in the addition of aromatic composition. The reason of this could be a result of the Hydrodeoxygenation and Hydrogenation on transition metals. The increasing behavior of aromatic elements can be observed in various groups, especially 5% wt. Ni/HZSM-5, which contains significantly high in phenol composition, possibly due to the behavior of the catalyst type with 5%wt. Ni/HZSM-5. Additionally, the pyrolysis state has a substantial effect on a rise in the phenolic constituents. The research conducted by Iliopoulou *et al.* (2012) shows the same behavioral effects of increasing this phenolic constituent; however, there have been no definitive studies on the exact cause.

Table 3 Classification of functions group within the bio-oil of each catalyst from GC-MS from the MCR at 450°C, Cat./Husk 0.05, 1.6-2.8 mm, 90 min.

Functional Group	**(wt% of Aromatic in bio-oil)**							
	Without catalyst	**HZSM-5.**	**10%wt.Co /HZSM-5**	**10%wt.Ni /HZSM-5**	**5%wt.Co /HZSM-5**	**5%wt.Ni /HZSM-5**	**2%wt.Co /HZSM-5**	**2%wt.Ni /HZSM-5**
Furan	4.77	6.24	5.94	5.43	4.48	5.13	4.83	6.13
Alcohol / Ether	4.55	11.54	4.98	15.21	7.1	5.76	9.45	10.23
Phenol	13.54	15.22	17.87	12.61	18.34	22.19	14.97	18.53
Ketones / Aldehydes	0	0.5	2.86	0	0.36	0.52	0.92	0.24
Acid / ester	0.16	0.58	1.68	0.28	2.31	0	0.95	0
Amines / amides	8.17	3.97	3.17	4.91	2.94	2.91	2.57	3.33
Alken / Alken / Alkyne	0	0	0.24	0	0	0.26	0.25	0
All	31.19	38.05	36.74	38.44	35.53	36.77	33.94	38.46

Since the amount of aromatic components cannot be directly compared to the potential of bio-oil; however, this can only illustrate the preliminary overall trends (Fan *et al*., 2014). Therefore, aromatic yields are determined according to Eq.4 with the aim of measuring the potential of the catalyst being used in the next experiment.

According to the calculation shown in Figure 6, the total yield of aromatic in bio-oils from each the MCR of catalyst at 450°C, Cat./Husk of 0.05, the size of 1.6-2.8 mm. In the case of catalysts 2, 5, 10%wt. Co/HZSM-5, it can be found that the aromatic composition of bio-oil is approximately at 13.63 wt%, 15.05 wt%, and 19.02 wt% respectively. While the aromatic components of bio-oil for the case of catalysts 2, 5, 10% wt. Ni/HZSM-5 are around 18.85 wt%, 16.4 wt%, and 17.91 wt% respectively. From the experimental results where the content of cobalt metals is increased, it can be seen that there is also a rise in the aromatic yield with the exception of the case for 2%wt. Ni/HZSM-5 which would possibly due to the assumption that the amount of 2 wt% Ni loading is appropriate for occuring the reaction which leads to the highest bio-oil yield, compared to the case for 5%wt. Ni/HZSM-5 and 10%wt. Ni/HZSM-5. However, there has been no evidence on approving the metal contents of 2%wt. Ni/HZSM-5.

Regarding Figure 6, it can be obtained that HZSM-5, 10%wt. Co/HZSM-5, 2%wt. Ni/HZSM-5 provide a similar yield of aromatic in bio-oil which is about 18.6, 19.02, and 18.85 respectively. In relation to taking the valued substances in the furan group, the phenyl group, the amine/amide group, the alkane/alkene/alkyne group into consideration, it is observed that only 10%wt. Co/HZSM-5 and 2%wt. Ni/HZSM-5 have a similar aromatic yield and are higher than HZSM-5. However, the aromatic yield for 10%wt. Co/HZSM-5 is recorded to be the lowest when taking unwanted compounds, alcohol/ether, ketone/aldehyde, acid/ester into account. This would lead to considering 10%wt. Co/HZSM-5 for the next experiment.

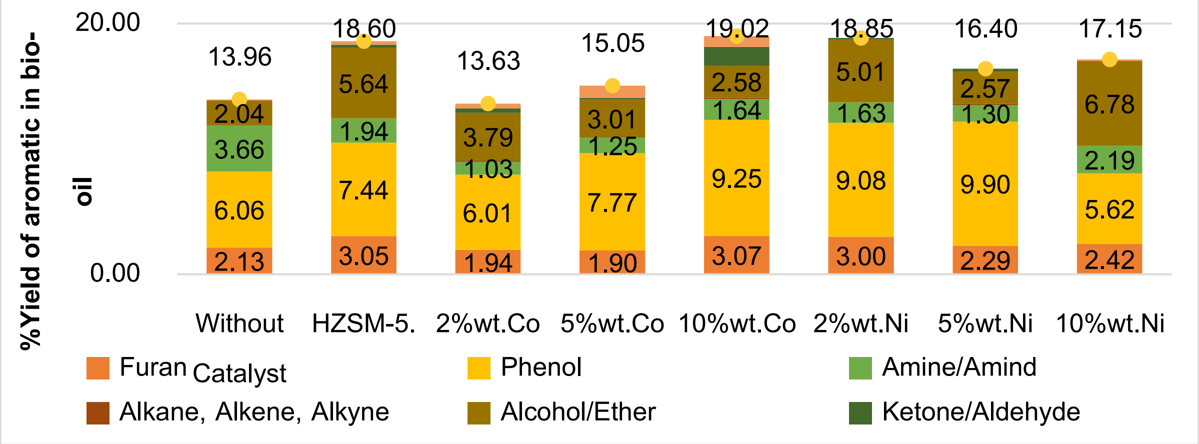

Figure 6 The total yield of aromatic in bio-oill from the MCR, at 450°C, Cat./Husk 0.05, 1.6-2.8 mm, 90 min.

3.5 ANOVA analysis results of bio-oil

Box-Behnken design experiments with the State-Ease Design Expert program are used for design and statistical studies by assigning three independent variables, where each variable has three levels which are temperature, Cat./Husk, and size ,as defined to be A, B, and C variables respectively. Each variable is observed to be an important variable affecting the yield of bio-oil (Mutsengerere *et al*., 2019). The result shown in Table 4 illustrates the experimental conditions by BBD. It can be seen that the result can predict not only the yield of bio-oil in theory which is similar to reality, but also the impact and response of variables influencing the yield of bio-oil.

Table 4 The experimental conditions for the appropriate yield of bio-oil

Run	Factor 1	Factor 2	Factor 3	Response 1	Response 2
	A: Temperature, Celsius	B: Cat./Husk	C: Size, mm	%Yield of bio-oil,	%Yield of total Aromatic
1	350	0.05	1	24.34	8.32
2	425	0.07	1	40.06	17.74
3	425	0.05	0	34.41	9.96
4	425	0.03	1	32.33	10.76
5	350	0.05	-1	37.09	12.48
6	500	0.03	0	42.12	12.34
7	500	0.07	0	44.18	14.76
8	350	0.03	0	44.50	14.02
9	500	0.05	-1	29.90	12.11
10	500	0.05	1	44.59	13.49
11	350	0.07	0	42.08	14.47
12	425	0.05	0	34.32	9.94
13	425	0.05	0	38.10	11.03
14	425	0.03	-1	40.60	14.21
15	425	0.07	-1	35.71	12.91

Table 5 ANOVA analysis of the yield of bio-oil

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	446.19	9	49.58	6.68	0.0250	significant
A-Temp	20.39	1	20.39	2.75	0.1583	
B-Cat./Husk	0.77	1	0.77	0.10	0.7607	
C-Size	0.50	1	0.50	0.067	0.8057	
AB	5.02	1	5.02	0.68	0.4482	
AC	188.27	1	188.27	25.37	0.0040	significant
BC	39.83	1	39.83	5.37	0.0683	
A^2	18.02	1	18.02	2.43	0.1800	
B^2	107.81	1	107.81	14.53	0.0125	significant
C^2	54.37	1	54.37	7.33	0.0424	significant
R-Squared	0.9232		Std. Dev.	2.72		
Adj R-Squared	0.7850		Mean	37.62	C.V. %	7.24

ANOVA analysis is used to prove the model for the yield of bio-oil, which is identified as a quadratic model. The relatively high Fischer test value (F-Value) can explain the reliability of the equation. In addition to this, the lower the p-value indicates how the equation is important to the yield of bio-oil.

Yield-Bio-oil = 146.36 - 0.3498A - 1652.86B - 47.0152C + 0.74697AB + 0.0915AC + 157.78BC + 0.000393A ^ 2 + 13508.938B ^ 2 - 3.837C ^ 2 (6)

Eq. 6 can predict the behavior of bio-oil production. The signifiant parameters affecting the yield of bio-oil are determined by the P-value, which needs to be less than 0.05 where this indicator represents the important variables.

According to Table 5, the results of ANOVA analysis of the yield of bio-oil, the temperature and husk size (AC), the catalyst/husk content (B^2), and the coffee husk size (C^2) are significant variables influencing the yield of bio-oil.

The R-Squared coefficient of the yield of bio-oil is 0.9232, indicating a variance of the equation to be 98.30%. The Adj R-Squared value of the yield of bio-oil is 0.7850, which indicates that the experimental results are close to 78.5% between experimental and theoretical values. Not only this, these results express that the the number of experimental variables are excessive, which some of the variables are not essential and influential with respect to the yield of bio-oil, resulting in lower Adj R-Squared values. The standard deviation of the yield of bio-oil is 2.72. The mean value of the yield of bio-oil is 37.62. The Coefficient of variation (CV%) of the yield of bio-oil is 7.24, which is observed to be low CV% (<10%), leading to higher reliability and good reproducibility of the regression model. (Gupta & Mondal, 2019).

The key parameters affecting bio-oil yield are determined by the P-value, which must be less than 0.05. The AC, B^2, C^2 variables provide P-values to 0.0040, 0.0125, and 0.0424 respectively.

Figure 7 illustrates the relationship between the temperature and the size of the coffee husk (AC variable) and the yield of bio-oil. If the size of the coffee husk increases, the temperature will also increase in order to obtain higher yield of bio-oil. In a similar way, when the coffee husk experiences a drop in its size, the temperature using in the process will also decrease.

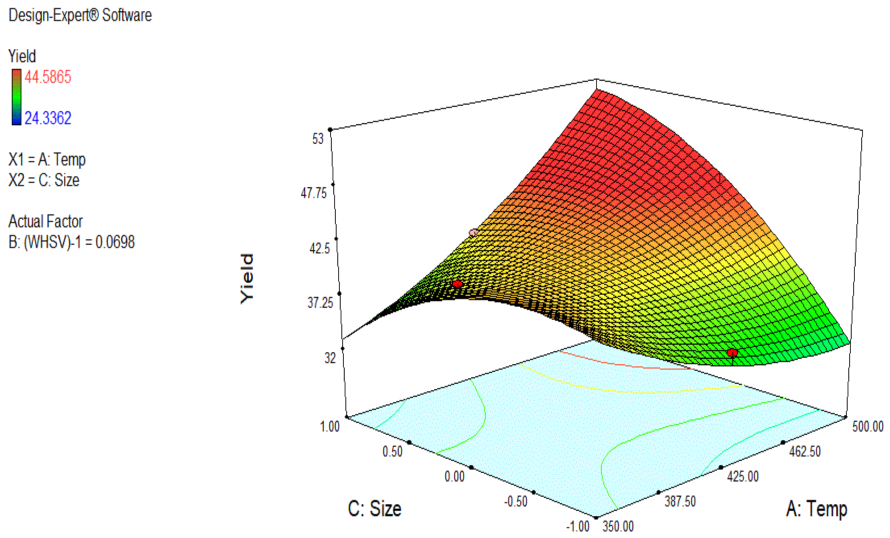

Figure 7 The relationship between temperature and size of the coffee husk (AC variable) and the yield of bio-oil

Figure **8** shows the relationship of Cat./Husk (variable B), the size of the coffee husk (C variable) and the yield of bio-oil with the yield of bio-oil. If Cat./Husk increases, the yield of bio-oil also increases. In relation to the size of the coffee husk (C variable) and the yield of bio-oil, if the coffee husk is large, high temperature will be required. On the other hand, when the size of the husk is small, it is not necessary that the temperature must be high, depending on the size of the coffee husk

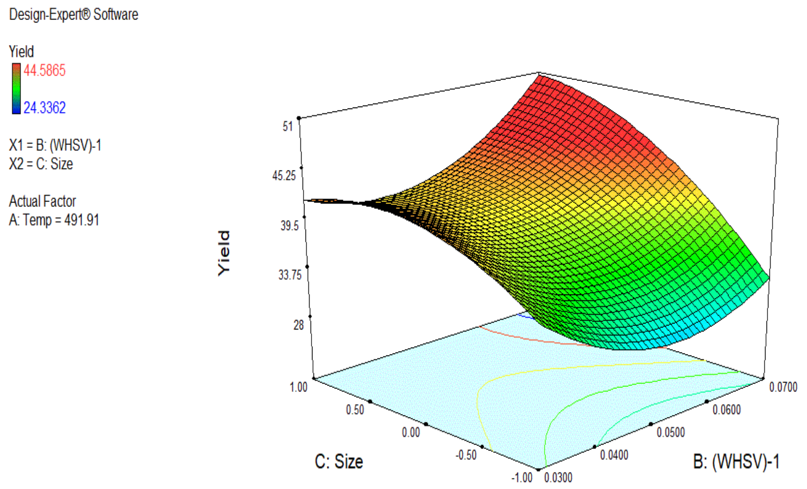

Figure 8 The relationship of Cat./Husk (B variable), the coffee husk size (C variable) and the yield of bio-oil

Regarding Eq.7, a high temperature, a high catalyst/husk, and a low husk size are required in order to obtaining the high yield of bio-oil. However, according to a report carried out by Iliopoulou *et al.* (2012), the small size of the biomass causes the coke to clog the pores of the catalyst, which means that the size of the coffee husk should be large

$$\text{Yield-Bio-oil} = 146.36 + 0.0915AC + 13508.938B^2 - 3.837C^2 \quad (7)$$

3.6 The Optimal Reaction Conditions

Design Expert 6.0.6 software is used for fitting the developed equations, determining and assessing the statistical significance of the equations. Therefore, referred to the experiment in Section 3.5, Design-Expert software uses statistics from the data of influences and variables for analysis to determine the optimal conditions for high bio-oil yield and high aromatic yield in the bio-oil. (Ismail *et al.*, 2013)

All independent variables and response results have been appropriately set. The desired setting conditions are specified in Table 6 with the aim of acquiring a high yield of bio-oil and high yield of aromatic in bio-oil (Gupta & Mondal, 2019). The most suitable condition, being theoretically used, is the temperature of 450.93°C, Cat./Husk of 0.07 and the coffee husk size of 2.8-4 mm. At this condition, the prediction related to the yield of bio-oil and a total aromatic yield in the equation is 43.97 wt% and 17.74 wt% respectively. The results of the GC-MS analysis is observed to be the complexity of bio-oil products from pyrolysis, which is a result of the decomposition of cellulose, hemicellulose and lignin as found in the components of traditional biomass raw materials. According to the experimental results, an amount of acid and phenol is around 20.59 wt% and 10.09% wt respectively. Not only this, functional group such as alcohol and ether is found to be 5 wt%. Other compounds are as follows: amines and amides of 3.59 wt%, furan of 3.76 wt%, ketones and aldehydes of 1.56 wt%. The discovered components, such as pyridine, an aromatic component of the amine and amide function groups, have relatively high market prices, including furen and phenol alcohol.

Table 6 Goals set for independent variables and numerical optimization responses

Name	Goal	Lower Limit	Upper Limit	Solutions
Temperature (°C)	is in range	350	500	450.93
Cat./Husk	is in range	0.0300	0.0700	0.07
Size (mm)	is in range	-1	1	1
Yield of bio-oil (wt%)	maximize	24.34	44.59	43.97
Yield of total aromatic (wt%)	maximize	8.32	17.74	17.74

Table 7 Composition in bio-oil analyzed by GC-MS at 500°C, Cat./Husk is 0.07, size 2.8-4 mm.

Function Group	Name of substance	%peak area	wt%
	Furan	7.61	3.76
	2-furan-carboxaldehyde	2.59	1.28
	2(3H)-Furanone, dihydro-	1.18	0.58
	3-Furanmethanol	2.8	1.38
	Alcohol/ether	10.21	5.05
Aliphatic		8.54	4.22
	2-Propanone, 1-hydroxy-	5.23	2.59
	1-Hydroxybutan-2-one	1.42	0.70
Aromatic		1.67	0.83
	1-(3,4-Dimethoxyphenyl)-1-ethanol	0.82	0.41
	Benzene methanol	0.85	0.42
	Phenol	20.39	10.09
	Phenol, 2-methoxy-	5.29	2.62
	Phenol	3.96	1.96
	Guaiacol, 4-ethyl-	1.56	0.78
	Phenol, 2,6-dimethoxy-	2.72	1.35
	5-Hydroxy-4-methoxy-1,3-benzodioxole	1.33	0.66
	Creosol	1.83	0.91
	Ketone/Aldehyde	3.15	1.56
Aliphatic		3.15	1.56
	2-Cyclopenten-1-one, 3-methyl-	0.98	0.48
	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	1.04	0.51
	Acid/Ester	41.63	20.59
Aliphatic		40.72	20.14
	Acetic acid	37.97	18.78
	Propanoic acid	2.37	1.17
Aromatic		0.66	0.32
	4-Methyl-1-(acetoxy)benzene	0.66	0.33
	Amine/Amide	7.25	3.59
Aliphatic		2.97	1.47
	1H-Purine-2,6-dione, 3,7-dihydro-1,3,7-trimethyl-	2.97	1.47
Aromatic		4.28	2.12
	Pyridine	2.16	1.07
	1,2,4,5-Tetrazine	1.37	0.68
	Alkane, Alkene, Alkyne (Aliphatic)	1.08	0.53
15.8167	Ethene, fluoro-	0.52	0.26
18.3748	Cyclobutane, 1,3-difluoro-1,3-dimethyl-, cis-	0.56	0.28

Conclusions

In relation to specifying the characteristics of the coffee husks and their trace elements, it can be proved that the coffee husk is potentially capable of performing biomass into the process of bio-oil production. Although this could not be high efficiency based on the yield of product at this moment.

Catalyst improvement is achieved by adding cobalt and nickel loaded on HZSM-5, since the behavior of the metal towards HZSM-5 appears to be different resulting in the different response on the support. During the preparation process, losses may also occur due to the dry impregnation method.

The bio-oil production of coffee husk by the FBR and the MCR has been investigated. It can be seen that the coffee husk bio-oil with a 10 %wt. Co/HZSM-5 catalyst from the MCR has the highest bio-oil yield of 51.76 wt% and the aromatic yield of 19.02 %wt. The results show that using the MCR as a reactor is far more efficient method to produce the bio-oil, compared to FBR. This is the effect of radiative heating, which provides direct molecular vibrations of microwave. It is observed that different types of catalysts and Cat./Husk ratio also affect the yield of bio-oil and the yield of aromatic in the bio-oil.

By simulating the experiment using response surface method (RSM) with Box-Behnken design (BBD) using 10% wt.Co/HZSM-5 and the MCR, the variables influencing the effect of bio-oil yield are temperature and husk size (AC variable), Catalyst/Husk (B variable), and coffee husk size (C variable). The higher yield of bio-oil would be obtained from the higher the AC, B and C variables. The small size of the coffee husk causes the coke to clog the pores of the catalyst. The experiment indicates that the optimum condition for bio-oil production is at temperature of 450°C, Catalyst/Husk of 0.07, the size of 2.8 mm, leading to 43.97 wt% of bio-oil yield and 17.74 wt% of aromatic yield in bio-oil.

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