

Catalytic Cracking of Pyrolysis Oil Derived from Rubberwood to Produce Green Gasoline Components

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An attempt was made to generate gasoline-range aromatics from pyrolysis oil derived from rubberwood. Catalytic cracking of the pyrolysis oil was conducted using an HZSM-5 catalyst in a dual reactor. The effects of reaction temperature, catalyst weight, and nitrogen flow rate were investigated to determine the yield of organic liquid product (OLP) and the percentage of gasoline aromatics in the OLP. The results showed that the maximum OLP yield was about 13.6 wt%, which was achieved at 511 °C, a catalyst weight of 3.2 g, and an N₂ flow rate of 3 mL/min. The maximum percentage of gasoline aromatics was about 27 wt%, which was obtained at 595 °C, a catalyst weight of 5 g, and an N₂ flow rate of 3 mL/min. Although the yield of gasoline aromatics was low, the expected components were detected in the OLP, including benzene, toluene, ethyl benzene, and xylenes (BTEX). These findings demonstrated that green gasoline aromatics can be produced from rubberwood pyrolysis oil *via* zeolite cracking.

Keywords: Pyrolysis oil; Zeolite cracking; Organic liquid product (OLP); Green gasoline-range aromatics

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INTRODUCTION

Biomass represents a potential alternative source of energy, which is an important complement to fossil fuels. As such, it attracted significant attention as a renewable source of energy after the global oil crisis of the 1970s (Demirbas 2007; Lucia 2008; Demirbas *et al.* 2009). In addition, biomass currently is considered to be the only sustainable source that can be used to produce energy-related products, including electricity, heat, and valuable chemicals such as resins, flavorings, and other materials (Huber *et al.* 2006; Dodds and Gross 2007).

The first generation of biofuels were primarily bioethanol and biodiesel made from sugar, starch, and vegetable oil. To date, such biofuels have been widely produced across several countries and continents, notably Brazil, South America, Europe, and the United States (Charles *et al.* 2007; Mojoviä *et al.* 2009); however, they have been produced from food-grade biomass, which could lead to critical concerns related to food security (Gronowska *et al.* 2009). Therefore, it is very important to be able to produce biofuels from non-food resources such as ligno-cellulosic materials: wood chips, switch grasses and most importantly agricultural wastes, such as sugarcane bagasse, corn stover and rice straw.

Pyrolysis oils derived from wood-based biomass are one of the most promising renewable fuels. They are environmentally-friendly candidates because they contain a low content of sulfur compared to fossil-derived oils (Czernik and Bridgwater 2004). Recently, extensive attention has been focused on the technology of fast pyrolysis rather than slow pyrolysis, as the former produces high yield of pyrolysis oil with low water content in a

short residence time; however, this technology is still not fully developed regarding its commercial applications. Correspondingly, the slow pyrolysis technology produces a low yield of oil with high water content in a long residence time; however, this technology is known to have been practiced for ages to enhance char production (Bridgwater and Peacocke 2000; Stevens and Brown 2011). Fast pyrolysis process, nonetheless, seems to be superior for the preparation of biofuel.

Pyrolysis oil has attracted considerable interest due to its many applications in industry. Even though pyrolysis oil has been shown to be an alternative to petroleum fuels, it also has potential for use in producing value-added chemicals for the pharmaceutical, food, and paint industries (Bridgwater and Grassi 1991; Chiamonti *et al.* 2007). However, the direct substitution of pyrolysis oil for petroleum and other chemicals might be limited due to its thermal instability, high viscosity, and high oxygen content (Czernik and Bridgwater 2004; Mohan *et al.* 2006). As a result, before the pyrolysis oil can be used, an upgrading process is required to improve its quality by reducing the oxygen content (Zhang *et al.* 2007). Catalytic cracking and hydrotreating are two routes that have been used to upgrade the oil. The latter (named hydro-deoxygenation) is a deoxygenation process performed under high pressure of hydrogen; it has been studied recently for upgrading liquefied biomass obtained with the low-temperature liquefaction, which is a promising thermochemical route that uses less energy as compared to the pyrolysis technology. Related studies regarding the hydro-deoxygenation of liquefied biomass were reported by Grilc *et al.* (2014, 2015). The hydro-deoxygenation process, therefore, is considered as a vital process in the upgrading of biomass, perhaps even more so than cracking. However, catalytic cracking might be preferred because it has some significant advantages, *i.e.*, it does not require hydrogen, operates at atmospheric pressure, and has a lower operating cost (Huber and Corma 2007). Consequently, the zeolite cracking of pyrolysis oils to fuels and chemicals using HZSM-5 zeolite catalysts, which promote deoxygenation reactions, has attracted significant attention in recent years (Vitolo *et al.* 2001).

Presently, the concern of producing green gasoline, particularly gasoline-range aromatics from pyrolysis oil, has aroused attention. Previous studies have demonstrated that gasoline-range hydrocarbons can be produced from pyrolysis oil by catalytic cracking over HZSM-5 catalyst. Adjaye and Bakhshi (1995b,c) conducted extensive studies of the conversion of pyrolysis oil derived from maplewood to liquid products that had high concentrations of gasoline-range hydrocarbons. In their study, different zeolite catalysts were investigated for their relative performance in upgrading the pyrolysis oil, and the results showed that HZSM-5 was the most effective catalyst and gave a high yield of gasoline hydrocarbons, principally made up of BTEX aromatics.

A similar study was reported by Vitolo *et al.* (1999), who attempted to upgrade different pyrolysis oils derived from oak, pine, and a mixture of both using HZSM-5 and H-Y zeolites. Their findings showed that an HZSM-5 catalyst could be used to upgrade the pyrolysis oil and produce clear, separable oil, whereas the H-Y zeolites produced a single phase of aqueous liquid. The oils obtained by upgrading oak-derived pyrolysis oil at a different temperatures using HZSM-5, contained an elevated percentage of aromatics, including benzene, toluene, ethylbenzene, xylenes, and trimethylbenzenes. Furthermore, the upgraded oils showed a higher degree of deoxygenation with a quite high heating value and a good combustibility. The upgrading of pyrolysis oil derived from rice husk was investigated by Wang *et al.* (2013). They outlined a unique technique to produce high-quality gasoline rich with aromatic hydrocarbons by using a distilled fraction of the

pyrolysis oil with ethanol and investigated their co-cracking behaviour using the HZSM-5 catalyst.

Recently, Bi and co-workers (2013) explored an innovative cracking technique based on the residual heavy fraction (tar) of pyrolysis oil derived from straw stalks; with their technique they could increase the efficiency and selectivity of producing aromatics by passing an electric current through the catalytic reactor. The current promoted the deoxygenation and cracking reactions efficiently, giving higher yield of aromatics (mainly consisted of BTEX) as compared to those produced by the conventional catalytic conversion without current. Interestingly, it was found that, among the catalysts used in the study, HZSM-5 was the most effective and obtained the highest yield of aromatic hydrocarbons.

The rubber tree is widely planted in southern Thailand (Krukanont and Prasertsan 2004) and has been utilized to a great extent for charcoal production using the slow-pyrolysis process. The pyrolysis liquid is obtained as a by-product during the manufacture of charcoal, and it is used extensively in plant growth and protection, particularly in pesticide applications (Tiilikkala *et al.* 2010).

It would be highly desirable to get more exploitation to the pyrolysis liquid, as it will clearly add value to the production of charcoal. To the best of the authors' knowledge, pyrolysis liquid derived as a by-product from rubberwood has received limited attention, and no study has been conducted to upgrade it to gasoline-range aromatics or organic liquid product (OLP). Thus in this work, the catalytic conversion of pyrolysis liquid after treatment was investigated, and its viability for producing gasoline-range aromatics was studied.

In this paper, catalytic cracking of rubberwood-derived oil over HZSM-5 catalyst was conducted in a dual-reaction system. The effect of operating conditions on the yield of OLP and the percentage of gasoline aromatics in the OLP was investigated. The optimum operating conditions were analyzed using design of experiments (DOE) and response surface methodology (RSM).

EXPERIMENTAL

Materials

Preparation and characterization of pyrolysis oil

Crude pyrolysis liquid was treated to reduce water by evaporation. The concentrated liquid was then labelled as pyrolysis oil (Saad and Ratanwilia 2014). The concentrated liquid produced in the evaporation process was labelled as pyrolysis oil. Table 1 gives important characteristics of pyrolysis oil, such as water content, specific gravity, heating value, pH, and elemental content. The table also identifies the instruments used in analysis.

The chemical composition was identified using a gas chromatography mass spectrometry system (Trace GC Ultra/ISQMST) equipped with a capillary column of 30 m long \times 0.25 mm \times 0.25 μ m film thickness. The GC oven temperature was kept at 35 °C for 5 min, and programmed to increase from 35 to 245 °C at the rate of 4 °C/min. The data was acquired with Xcalibur software using the Wiley mass spectra library. Table 2 shows the chemical composition of the pyrolysis oil.

Table 1. Physical Characteristics and Elemental Analysis of Pyrolysis Oil

	Typical Value	Instrument
Water content (wt%)	30.00	Coulometric Karl Fischer titrator, Mettler Toledo DL 39, Taiwan.
Specific gravity	1.22	Specific Gravity Bottle.
Gross heating value (MJ/kg)	22.00	CHNS/O Analyzer, Flash EA 1112 Series, Thermo Quest, Italy.
Net heating value (MJ/kg)	21.00	<i>Automatic calculation of GHV (Gross Heat Value) and NHV (Net Heat Value) using Eager 300 software.</i>
pH	3.72	Docu-pH+ meter, Sartorius Mechatronics, Germany.
Elemental composition (wt%)		CHNS/O Analyzer, Flash EA 1112 Series, Thermo Quest, Italy.
C	47.37	
H	5.78	
O	23.58	
N	1.26	

The conducted tests underwent duplicate runs to determine repeatability. The experimental error was less than 3.5%

Table 2. Chemical Composition of the Pyrolysis Oil Identified by GC–MS

	Composition	MW	Formula	Peak area % ^a
1	Acetic acid	60	C ₂ H ₄ O ₂	32.65
2	Syringol	154	C ₈ H ₁₀ O ₃	13.36
3	Corylon	112	C ₆ H ₈ O ₂	8.62
4	4-Methoxy-3-(methoxymethyl)phenol	168	C ₉ H ₁₂ O ₃	4.28
5	Acetol	74	C ₃ H ₆ O ₂	4.08
6	4-Chlorobutyric acid	122	C ₄ H ₇ ClO ₂	3.09
7	Phenol	94	C ₆ H ₆ O	2.13
8	2,6-Dihydroxy-4-methoxyacetophenone	182	C ₉ H ₁₀ O ₄	2.02
9	Butyryl oxide	158	C ₈ H ₁₄ O ₃	1.91
10	Anhydro sugar	132	C ₅ H ₈ O ₄	1.72
11	3-Pyridinol	95	C ₅ H ₅ NO	1.64
12	3,4,8-Trimethyl-2-none-1-ol	182	C ₁₂ H ₂₂ O	1.61
13	Syringyl acetone	126	C ₇ H ₁₀ O ₂	1.29
14	Ethyl cyclo pentenolone	180	C ₁₀ H ₁₂ O ₃	1.59
15	1-(4-Hydroxy-3-methoxyphenyl)acetone	166	C ₁₀ H ₁₄ O ₂	1.49
16	p-Butoxyphenol	210	C ₁₁ H ₁₄ O ₄	1.36
17	3,4-Anhydro-d-galactosan	144	C ₆ H ₈ O ₄	1.22
18	Levulinic acid	116	C ₅ H ₈ O ₃	1.18
19	à-Furanone	84	C ₄ H ₄ O ₂	1.18
20	2-hydroxy-4 6-dimethoxy acetophenone	196	C ₁₀ H ₁₂ O ₄	1.13
21	^b Unidentified			12.45

^a The composition of the pyrolysis oil was estimated by the peak area % of GC-MS
^b Determined by difference

Preparation and characterization of the catalyst

NH₄-ZSM-5 zeolite (CBV 3024E) was provided by Zeolyst International (USA) as a fine powder. Its surface area and SiO₂/Al₂O₃ ratio were 405 m²/g and 30, respectively. The HZSM-5 catalyst was prepared by removing the ammonia from NH₄-ZSM-5 by calcination at 550 °C for 5 h in a stream of nitrogen to obtain the protonic form, with stronger acid sites. The structure and composition of the catalyst were identified by an X-

ray diffraction (XRD; X'Pert MPD, PHILIPS), and the XRD patterns were found to be similar to the standard HZSM-5 zeolite reported by Treacy and Higgins (2007), as given in Fig. 1. The morphology and particle sizes were determined from the scanning electron microscopy (SEM) image taken with a JSM-5800 LV, JEOL, as shown in Fig 2.

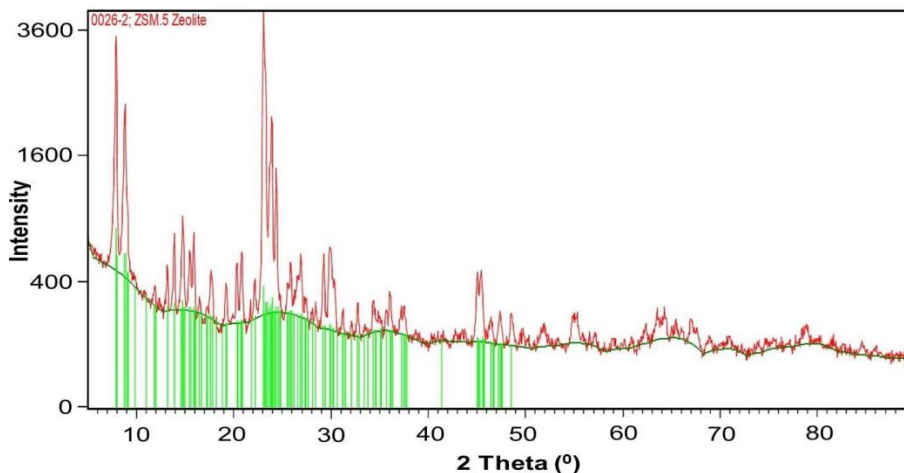


Fig. 1. XRD pattern of HZSM-5 catalyst

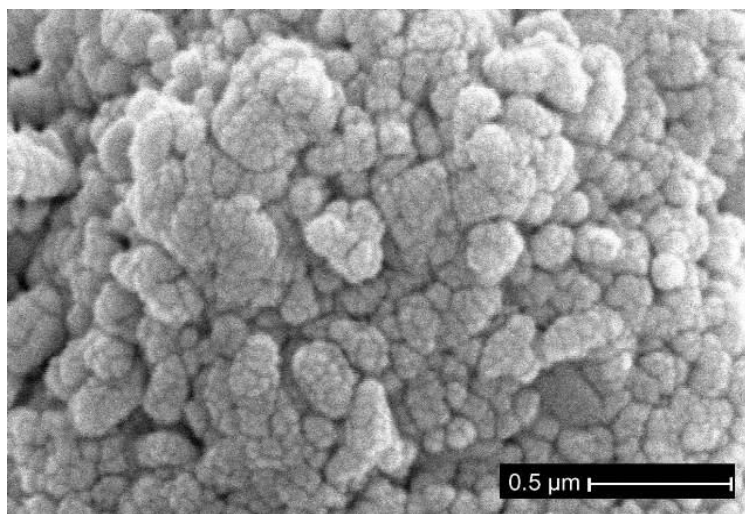


Fig. 2. SEM image for HZSM-5 catalyst

Methods

Experimental setup and procedure

The pyrolysis oil was cracked in a dual-reaction system without any catalyst in the first reactor, followed by a second fixed bed reactor loaded with HZSM-5 catalyst, as shown in Fig. 3. The reactors were stainless steel tubes with an inner diameter of 30 mm and lengths of 250 and 350 mm for the first and second reactors, respectively. The two reactors were placed coaxially in the furnaces. The dual reactor operation was studied previously (Sharma *et al.* 1993; Srinivas *et al.* 2000) in order to reduce coke formation during the process. It was found to be effective in enhancing the catalyst life by minimizing coking, hence reducing the frequency of catalyst regeneration. The experimental runs were conducted at atmospheric pressure in the dual reactor system, which was operated in the

temperature range of 400 to 600 °C with a catalyst weight of 1 to 5 g and a nitrogen flow rate of 3 to 10 mL/min.

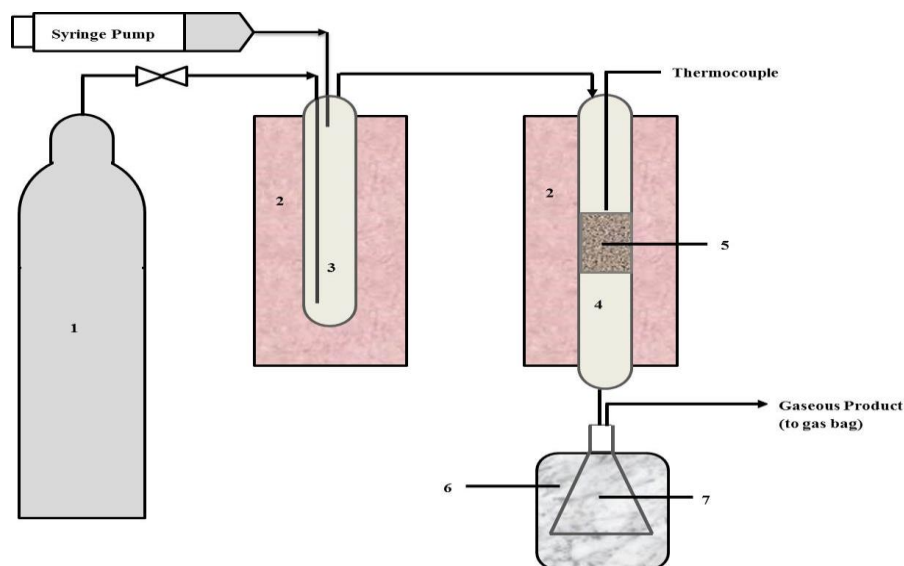


Fig. 3. Dual reactor setup showing (1) nitrogen cylinder, (2) furnace, (3) first reactor, (4) second reactor, (5) catalyst bed, (6) ice batch, (7) receiving flask

In a typical run, the second reactor was loaded with catalyst that was held on a plug of glass wool. The catalyst was weighed, and the values are provided in Table 3. Then, both reactors were heated in a stream of nitrogen until the desired temperature was attained, after which a syringe pump was used to introduce 15 g of pyrolysis oil into the first reactor at the rate of 1.4 g/min. The oil entered the first reactor together with the nitrogen carrier gas at different flow rates, as shown in Table 3. The oil was thermally cracked, and a significant amount of char was formed and deposited in the reactor. Then, the oil vapor flowed through the second reactor, passing the catalyst bed where the catalytic cracking of the oil vapor occurred. Some char was formed above the catalyst bed due to the thermal effect at the reactor's temperature. The products from the second reactor were cooled (collected in an ice-cooled flask) and separated into liquid and gaseous products. The liquid product was obtained in the form of immiscible layers, *i.e.*, an organic layer and an aqueous layer. The organic layer, *i.e.*, the OLP, was drawn off from the aqueous layer with a syringe. The amounts of OLP and aqueous liquid were determined by the difference in weight of the liquid product before and after the aqueous and organic layers were separated. In addition, the uncondensed gaseous product was collected in a gas bag, and its weight was estimated by the difference in weight of the bag before and after removing the gas, excluding the amount of N₂. Each experimental run lasted for about 1.30 h, because it was observed that the formation of products decreased significantly after 1.30 h for all runs.

After each run, the char formed in the first reactor was removed and weighed. The spent catalyst, tar, and the char deposited above the catalyst bed were removed from the second reactor. The inner surface of the reactor and the catalyst were washed with methanol to remove the tar. The washed catalyst was later dried at 100 °C overnight and then heated in air at 550 °C for 5 h in order to determine the weight of coke, which was determined by the difference in the weight of the catalyst before and after heating.

In addition, the yields of OLP, aqueous liquid, char, and gas relative to the total amount of pyrolysis oil feed were determined using the following relationship,

$$\text{Yield (wt\%)} = (P \times 100) / \text{pyrolysis oil fed (15 g)} \quad (1)$$

where P is the number of grams of product, *i.e.*, OLP, aqueous liquid, char, or gas.

Analysis of the liquid product

The liquid product included a separable oil layer (OLP) and an aqueous product. In this study, the product of interest was the gasoline fraction formed in the OLP, particularly gasoline-range aromatics, *i.e.*, benzene, toluene, ethylbenzene, and xylenes (BTEX), which were anticipated to have higher octane ratings (Diebold and Scahill 1988). Thus, only the gasoline hydrocarbons of BTEX were identified using gas chromatography (GC). The GC was equipped with a 30-m long, fused-silica capillary column and a flame ionization detector (FID). The oven temperature was programmed to increase from 40 to 250 °C. The identities of the peaks were determined by using BTEX standards, and the quantities were determined from a calibration curve that had been developed using the BTEX standard.

The aqueous product contained 78 to 85 wt% water, as determined by Karl Fischer titration, and it was expected to contain some water-soluble organic components, such as carboxylic acids, alcohols, and phenols. Then, a pH meter was used to attain the pH values, which ranged from 2.90 to 3.65.

Table 3. Experimental Design Matrix and Results

Runs	Experimental design			Experimental Results	
	Temperature °C	Catalyst g	N ₂ flow rate mL/min	OLP yield	Percentage of gasoline aromatics in OLP
1	400	1	6.5	5.80	0.34
2	400	3	3.0	11.27	0.62
3	400	3	10	11.07	0.57
4	400	5	6.5	11.33	1.43
5	500	1	3.0	12.13	6.69
6	500	1	10	12.00	6.48
7	500	3	6.5	13.20	17.11
8	500	3	6.5	13.13	17.25
9	500	3	6.5	13.33	18.06
10	500	5	3.0	12.47	23.81
11	500	5	10	12.33	23.10
12	600	1	6.5	12.27	6.71
13	600	3	3.0	11.53	26.41
14	600	3	10	11.40	22.02
15	600	5	6.5	10.00	19.95

The experiments were performed in duplicate (except the central points) for reproducibility check. The errors were found to be <3% in all the runs

Experimental Design and Response Surface Methodology

Response surface methodology (RSM) is one of the techniques used for designing experiments and developing an adequate mathematical model to predict the optimal values of independent variables (Cornell 1990; Clarke and Kempson 1997; Montgomery 2001).

In this study, the experiments were designed using Essential Regression and Experimental Design software. Three factors, *i.e.*, temperature (°C), the catalyst's weight

(g), and the flow rate of N₂ (mL/min), were chosen as the independent variables that would affect the catalytic cracking of the pyrolysis oil. The ranges of these factors included three levels, *i.e.*, low, central, and high. 15 experimental runs were designed using Box-Behnken with three center points as shown in Table 3.

Since OLP and gasoline aromatics were the most desired products, the experiments were conducted to determine two quantities (responses) as shown in Table 3, *i.e.*, the yield of OLP and the percentage of gasoline aromatics in the OLP. The model used for predicting OLP yield and percentage of aromatics is a quadratic equation as represented by,

$$Y = b_0 + b_1T + b_2C + b_3G + b_4T^2 + b_5C^2 + b_6G^2 + b_7TC + b_8TG + b_9CG \quad (2)$$

where Y is the predicted response; $b_0, b_1, b_2, b_3, b_4, b_5, b_6, b_7, b_8,$ and b_9 are the regression coefficients; and $T, C,$ and G are the coded independent variables for temperature, catalyst's weight and N₂ flow rate, respectively. In order to determine the optimum operating conditions, the response surface analysis was performed by utilizing Essential Regression software to maximize the yield of OLP and the percentage of gasoline aromatics.

RESULTS AND DISCUSSION

Product Distribution

The cracking process generated six products: OLP, an aqueous product, char, tar, coke, and non-condensable gases. Table 4 provides the overall product distribution for each run. It was observed that a significant amount of char was formed in the first reactor, and a small amount of char was formed above the catalyst bed in the second reactor. These observations imply that the formation of char occurred due to the thermal effect on the unstable components of the pyrolysis oil, more to the point, because of polymerization and condensation reactions, which form large molecules that are insoluble and infusible. Nevertheless, as shown in Table 4 (the yield of char ranged from about 18 to 22 wt % over the 15 runs), there was a slight decrease in the formation of char with the increase of temperature, probably due to secondary reactions occurring such as gasification. A similar observation concerning the formation of char during the cracking of pyrolysis oil, and the effect of temperature on char formation was reported by Adjaye and Bakhshi (1995b). The aqueous product contained 78 to 81 wt% water, indicating that some oxygen was removed in the form of water (Adjaye and Bakhshi 1995c). The amount of aqueous product ranged from about 36 to 53 wt %.

It was important to investigate the distribution of OLP yield, which ranged from about 6 to 13 wt% over the experimental runs. At 400 °C (runs 1-4), it was noted that the yield values were low, but they began to increase at 500 °C (runs 5-9) and reached a maximum of about 13 wt%. It was observed that the OLP decreased when the temperature was increased from 500 to 600 °C (runs 10-15). Adjaye and Bakhshi (1995b) and Bi *et al.* (2013) reported similar observations during the upgrading of pyrolysis oil and tar by HZSM-5 catalyst. They stated that the yield of OLP decreased as the temperature increased, meaning that a higher temperature led to the additional cracking of OLP, forming more gaseous products.

Table 4. Overall Product Distribution (wt% of the feed) for 15 Experimental Runs

Runs	Products					
	Aqueous Liquid	Organic Liquid Product	Char ^a	Residue ^b	Gas	Unaccounted
	wt%					
1	38.33	5.80	22.00	13.20	4.07	16.60
2	36.33	11.27	22.13	12.33	4.33	13.60
3	36.20	11.07	22.00	12.47	4.53	13.73
4	38.00	11.33	22.00	11.20	5.2	12.27
5	40.00	12.13	19.80	10.93	5.33	11.80
6	39.33	12.00	19.00	11.00	5.53	13.13
7	45.00	13.20	19.20	10.47	5.67	6.47
8	45.40	13.13	19.13	10.47	5.67	6.20
9	44.93	13.33	19.20	10.00	5.73	6.80
10	46.53	12.47	19.80	9.87	6.07	5.27
11	45.33	12.33	18.87	9.80	6.2	7.47
12	46.67	12.27	17.67	9.80	6.33	7.27
13	51.33	11.53	17.80	9.67	6.47	3.20
14	50.00	11.40	17.67	9.53	6.53	4.87
15	53.33	10.00	17.73	9.33	6.67	2.93

^a Char formed in the first reactor
^b Residue is categorized as char and tar that were quantified in the second reactor
All the experiments were repeated in duplicate (except the central points) showing a good reproducibility with low experiment errors (1–5 %)

The major oxygenated compounds in the pyrolysis oil (Table 2) were acids, phenolic compounds, ketones, esters, aldehydes, and a few others. It is important to state that the conversion of most of these oxygenated compounds to OLP over the HZSM-5 catalyst was an indication of its ability to remove oxygen through complex reactions, such as deoxygenation, cracking, cyclization, aromatization, isomerization and polymerization reactions (Adjaye and Bakhshi 1995a; Valle *et al.* 2010; Gong *et al.* 2011; Mentzel and Holm 2011). The low yield of OLP (about 6 to 13 wt%) might be attributed to the high water content of the sample (30%) and the char formation (about 18 to 22 wt%). In addition, the yield of gas increased slightly with the reaction temperature and catalyst, showing a highest value of about 7 wt% at 600 °C, 5 g of catalyst and, 6.5 mL/min of N₂ gas. The lowest value was 4 wt% achieved at 400 °C, 1 g of catalyst, and 6.5 mL/min of N₂ gas.

Content of Gasoline-Range Aromatics in OLP

The composition of OLP, particularly gasoline-range aromatics (BTEX), was of prime interest. Gasoline aromatics were analyzed by GC-FID, and Table 5 shows their distributions for the experimental runs.

It was found that the percentage of gasoline aromatics in OLP for all runs ranged from about 0.34 to 26 wt%, with a maximum value of about 26 wt% at 600 °C, 3 g of catalyst and 3 mL/min of N₂ gas. The formation of aromatic hydrocarbons in OLP supported the hypothesis that the oxygenated compounds, particularly substituted phenols, in the pyrolysis oil can be converted into aromatic hydrocarbons by dehydroxylation, decarbonylation, and decarboxylation with the HZSM-5 catalyst (Carlson *et al.* 2009; Valle *et al.* 2010; Zhao *et al.* 2010; Cheng and Huber 2011). In addition, as the pyrolysis oil contained some acids, alcohols, aldehydes, ketones and esters, it was suggested that during

the conversion of these compounds, olefins were formed as intermediate products, and they underwent a variety of further reactions to yield aromatic hydrocarbons (Adjaye and Bakhshi 1995a). It was noted that the percentage of gasoline aromatics increased slightly, from 0.34 wt% to 1.43 wt%, as the amount of catalyst used was increased at a reaction temperature of 400 °C. Similarly, at 500 °C, the percentage of gasoline aromatics increased significantly, from about 7 wt% to 24 wt%. There was a dramatic increase of gasoline aromatics at 600 °C when 3 g of catalyst were used instead of 1 g. However, a slight decrease was noted when 5 g of catalyst were used due to the secondary conversion of the aromatics. In general, by considering the effect of catalysts on the formation of aromatics, it can be seen that the decrease of catalyst (the feed rate of pyrolysis oil was fixed) generally minimizes the reactants residence time in the catalyst bed, as a result deoxygenation and cracking reactions will decrease. Regarding the effect of temperature on the aromatics distribution, it was noteworthy to observe that, with increasing reaction temperature (at fixed amounts of 1g, 3 g and 5 g of catalyst), the formation of aromatics remarkably increased; therefore, it can be suggested that higher temperature enhances further elimination of groups from the primary heavier aromatics (such as demethylation of xylenes) to form mostly toluene and further to benzene. However, with increasing temperature from 500 °C to 600 °C at 5 g of catalyst, the aromatics slightly decreased from about 23 wt% to 20 wt% as a result of the secondary cracking of the aromatics. Likewise, in terms of selectivity, increasing the catalyst and temperature contributed effectively to increasing the aromatics selectivity. Furthermore, it is suggested that the presence of HZSM-5 catalyst which exhibit shape selectivity, enhances the formation of toluene, xylenes and substituted benzenes in the OLP. Related observations and detailed proposals of the reaction pathways were studied previously (Adjaye and Bakhshi 1995a; Li *et al.* 2012; Zhu *et al.* 2013).

Table 5. Composition of Gasoline Aromatics in the OLP

Runs	OLP yield	Benzene	Toluene	Ethyl benzene	Xylenes ^a	(gasoline aromatics) ^b
	wt%					
1	5.80	0.06	0.14	0.12	0.02	0.34
2	11.27	0.10	0.32	0.18	0.02	0.62
3	11.07	0.13	0.25	0.17	0.02	0.57
4	11.33	0.30	0.97	Trace	0.16	1.43
5	12.13	0.75	2.49	Trace	3.45	6.69
6	12.00	0.63	2.08	Trace	3.77	6.48
7	13.20	2.20	7.03	0.07	7.81	17.11
8	13.13	3.12	10.23	0.95	2.95	17.25
9	13.33	2.88	10.07	1.70	3.41	18.06
10	12.47	3.65	16.10	0.72	3.34	23.81
11	12.33	3.31	15.49	0.73	3.57	23.10
12	12.27	1.32	2.86	0.85	1.68	6.71
13	11.53	6.47	16.86	0.70	2.38	26.41
14	11.40	6.14	13.47	0.00	2.41	22.02
15	10.00	0.00	8.66	0.38	10.91	19.95

^a Xylenes= p. xylene, m. xylene, o. xylene

^b Summation of BTEX

The experiments were conducted in duplicate (except the central points) to check their reproducibility. The errors were found to be <3%

The percentage of gasoline aromatics generated in this study was about the same as that obtained by Park *et al.* (2010) for the catalytic upgrading of pyrolytic vapors derived from the sawdust of radiata pine.

Optimization

The main interests in this work were OLP and gasoline aromatics in the OLP; hence, the results of the investigation are reported for the effects of three variables on the yield of OLP and the percentage of gasoline aromatics. RSM was used to predict the optimum values of the three variables. A mathematical model was developed based on the experimental design performed initially by Essential Regression software, as listed in Table 3. The experimental data was used to develop a quadratic regression model to predict the OLP yield and the aromatic percentage in OLP as a function of the three parameters including temperature (T , °C), catalyst's weight (C , g), and N_2 flow rate (G , mL/min), which was given by:

$$Y_{OLP} = -60.92 + 0.250T + 6.962C - 0.301G - 0.00021T^2 + 0.01959C^2 + 0.01959G^2 - 0.00975TC \quad (3)$$

$$Y_{Aromatics} = -183.03 + 0.700T - 0.00065T^2 - 0.932C^2 + 0.01716TC - 0.00043TG \quad (4)$$

The analysis of variance (ANOVA) summarized in Table 6, demonstrated that the models were highly significant at 95% confidence level, with high F-Value and very low F-significance. The regression coefficients and P-values were also shown; the latter were used to check the significance of each coefficient. From the significance test, it was found that temperature (T) and catalyst's weight (C) were the most significant factors (p -values < 0.05) affecting the OLP yield and the aromatics percentage in OLP. Additionally, as can be seen in Fig. 4, the values predicted for OLP and gasoline aromatics by the mathematical model were in good agreement with the experimental results, confirming the fitness of the model. From the figure, the model's results fit well with the experimental results, as indicated by the determination coefficients (R^2) of 0.926 and 0.906 for the model's predictions of OLP yield and gasoline aromatics, respectively.

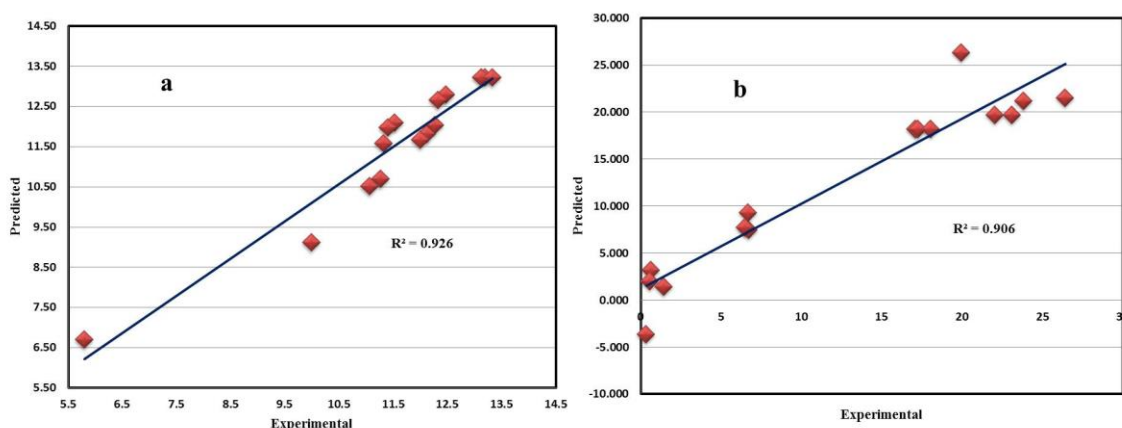


Fig. 4. Experimental results versus predicted values of (a) OLP yield and (b) gasoline aromatics (%) in OLP

Table 6. Analysis of Variance (ANOVA) for Quadratic Models

Source	Coefficient	P-value	Std Error	SS ^a	MS ^b	F-value	F-Significance	df ^c
Yield of OLP model								
b0	-60.92	0.00145	10.98					
b1	0.250	0.00083	0.04056					
b2	6.962	0.00082	1.125					
b3	-0.301	0.677	0.689					
b4	-0.00021	0.00162	3.94E-05					
b5	-0.307	0.02080	0.09862					
b6	0.01959	0.565	0.03220					
b7	-0.00975	0.00213	0.00190					
b8	5E-05	0.965	0.00108					
Regression				43.30	5.412	9.420	0.00677	8
Residual				3.447	0.575			6
LOF Error				3.427	0.857	83.174	0.01192	4
Pure Error				0.0206	0.0103			2
Total				46.74				14
Percentage of aromatics in OLP model								
b0	-183.03	0.00385	47.41					
b1	0.700	0.00542	0.192					
b2	-0.00065	0.00756	0.000192					
b3	-0.932	0.04863	0.409					
b4	0.01716	0.00737	0.00499					
b5	-0.00043	0.571	0.00074					
Regression				1187.8	237.57	17.30	0.000222	5
Residual				123.56	13.73			9
LOF Error				123.03	17.58	66.821	0.01482	7
Pure Error				0.526	0.263			2
Total				1311.4				14
^a SS= Sum of squares								
^b MS= Mean squares								
Confidence level= 95%								
^c df= Degree of freedom								

Essential Regression software was used to optimize the conditions, and the results showed that the maximum value of OLP yield was about 13.6 wt% for a temperature of 511 °C, a catalyst weight of 3.2 g, and an N₂ flow rate of 3 mL/min. Correspondingly, the maximum percentage of gasoline aromatics was about 27 wt%, which was obtained at 595 °C, a catalyst weight of 5 g, and an N₂ flow rate of 3 mL/min.

The three-dimensional (3D) response surfaces and their corresponding 2-D contours in Fig. 5, display the interaction effects of the most significant variables (temperature and catalyst weight) on the OLP yield and percentage of gasoline aromatics in OLP. The response surface can be used to determine the optimum levels of the parameters for the maximum response of OLP yield and aromatics percentage at the highest point of the surface. Fig. 5(A) shows the mutual effects of the temperature and catalyst weight on the OLP yield. The highest OLP yield was obtained at around 3 g of catalyst and decreased gradually to about 9 wt% with further increase of catalysts to about 5 g. However, there was a significant decrease in the OLP yield when the catalyst weight further decreased from 3 g to 1 g. This might be occurred due to less cracking of the pyrolysis oil. Also a highest OLP yield, i.e., about 13 wt%, was achieved at around 511 °C, then gradually dropped to about 11 wt% with increasing temperature to 600 °C due to an increased rate of cracking reactions, forming smaller compounds; however, an obvious

decrease of OLP yield was observed on lower temperatures as the cracking reactions do not take place efficiently at the lower temperatures. On the other hand, the mutual effects of the temperature and catalyst weight on the aromatics percentage were depicted in Fig. 5(B). This figure implies that a slight decrease in aromatics percentage occurred when the catalyst weight decreased from 5 g to about 3 g; however a significant drop of aromatics percentage was achieved at very low amount of catalysts. This can be explained by the impact of catalyst's acid sites, which are critical for maximizing aromatic percentage. So, as the amount of catalyst decreased (less acid sites), the formation of aromatics decreased. Likewise, the increase of coke deposition will lead to a blockage of the active sites, hence a decrease in the aromatics formation. Moreover, the aromatics percentage increased with increasing temperature, showing highest values at a temperature range of around 500 to 600 °C and thereafter decreased significantly at lower temperatures. The higher temperatures are usually required to thoroughly enhance deoxygenation reactions, to increase the aromatic formation.

The results from the response surface in Fig. 5(B) show that some values of aromatics percentage (optimum) lay beyond the independent variables, which indicate the need for further improved conditions.

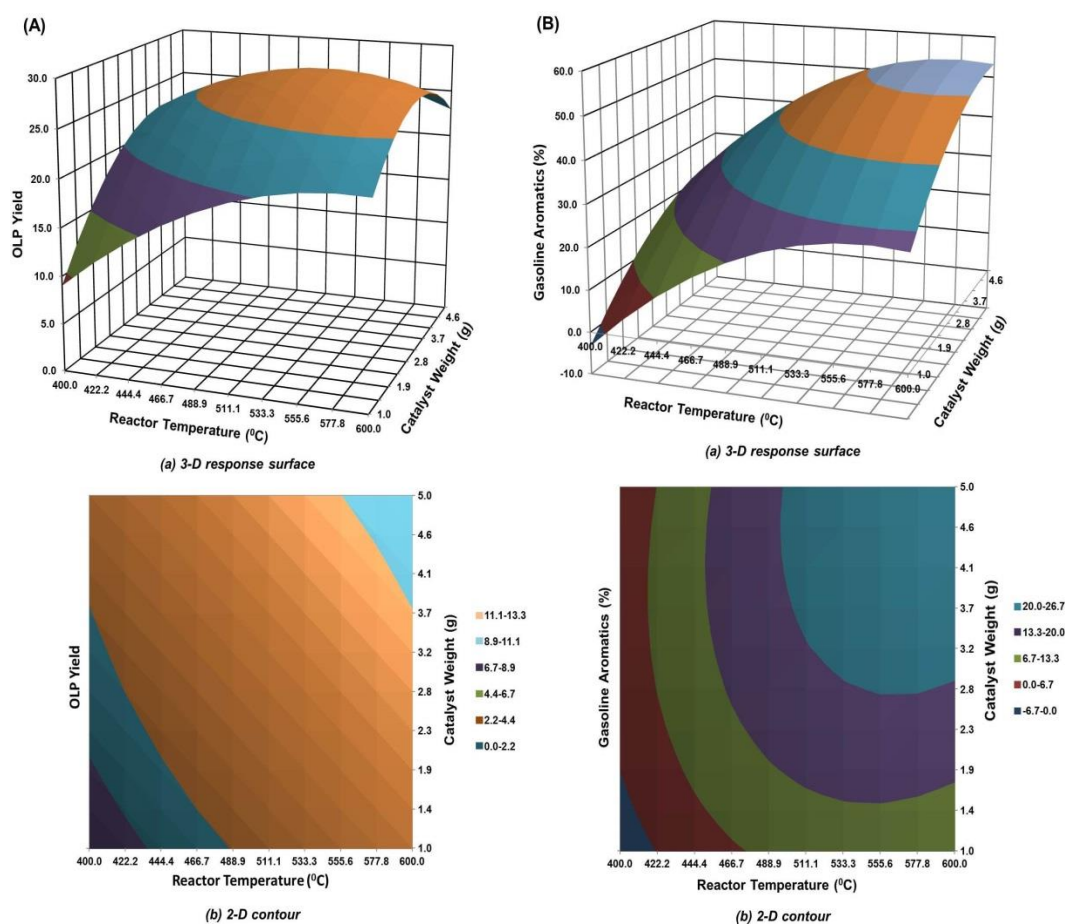


Fig. 5. Surface plot of: (A) OLP yield and (B) gasoline aromatics (%) in OLP as functions of catalyst weight and reactor temperature

The choice of the examined independent variables with their ranges seem appropriate with this process; however, the reduction of the feed rate (1.4 g/min) is most

likely needed, as it would probably enhance the catalyst cracking reactivity, hence increasing the aromatic concentration, which will therefore get the optimum values in the examined ranges.

The predicted results were validated by conducting experiments with the optimum conditions, as presented in Table 7. The yield of OLP was 15 wt%, whereas the predicted value was 13.6 wt%. The percentage of gasoline aromatics was 30 wt% compared to the predicted value of 27 wt%. The content of gasoline aromatics in OLP was identified, indicating that the content was dominated by toluene and that it had a very low percentage of ethylbenzene (Table 8). Furthermore, it was observed that the benzene concentration was somewhat less than the concentrations of toluene and xylenes, which indicated that benzene can be alkylated easily on the HSZM-5 catalyst due to its acidity (Chang *et al.* 1979; Bridgwater and Kuester 1988).

The BTEX are desirable chemicals that can be used as high octane gasoline additives. However, from environmental and safety viewpoints, benzene is not preferred due to its toxicity. As can be seen in Table 8, high amount of benzene was obtained in OLP, which is far from meeting gasoline specifications in the USA and Europe (Gibbs *et al.* 2009; Swick *et al.* 2014). Consequently, it would have to be recovered from toluene, xylenes, and ethylbenzene and used for chemicals production. Interestingly, BTEX also serve as important aromatic platforms, and they can provide feedstocks for producing a variety of chemicals, especially in the petrochemical industry.

Table 7. Predicted and Experimental Results at Optimum Conditions

	Predicted	Experiment	Optimum conditions		
			Temperature (°C)	Catalyst weight (g)	N ₂ flow rate (mL/min)
OLP yield (wt%)	13.6	15	511	3.2	3
Percentage of gasoline aromatics (wt%)	27	30	595	5	3

The values of the experimental results are average of duplicate trials with error <3

Table 8. Gasoline Aromatics Content in OLP at Optimum Conditions

	wt%
Benzene	5.16
Toluene	14.42
Ethylbenzene	0.58
Xylenes	9.84
Total	30.00

The values are average of duplicate trials with error <3

CONCLUSIONS

1. It was demonstrated that gasoline aromatics were generated from rubberwood-derived oil with concentration approaching 27 wt% in the OLP.
2. Temperature and catalyst weight were identified as the most significant factors affecting the OLP yield and the aromatics percentage in OLP. The model was adequate

for predicting the OLP yield and the percent of aromatics in OLP at less than 5% error. From RSM, a maximum value of 13.6 wt% of the OLP yield was obtained at 511 °C, 3.2 g of catalyst, and an N₂ flow rate of 3 mL/min, whereas the maximum percent of gasoline aromatics in the OLP. In other words, about 27 wt%, was achieved at 595 °C, 5 g of catalyst, and an N₂ flow rate of 3 mL/min.

3. Experiments were conducted at the optimum conditions in order to verify the accuracy of the simulated optimum conditions. The OLP yield was 15 wt% as compared to simulated value of 13.6 wt% (9.3% error). The percentage of gasoline aromatics was 30 wt% compared to simulated value of 27 wt% (10% error).
4. Among the side products, the bio-char seems the most important product, as it can be processed further for use as an adsorbent in a variety of applications.
5. It can be concluded that pyrolysis liquid obtained as a by-product of the production of charcoal from rubberwood has significant potential for use in producing gasoline since it contains BTEX components in the OLP.

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