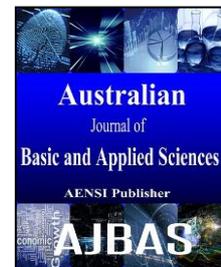




AUSTRALIAN JOURNAL OF BASIC AND APPLIED SCIENCES

ISSN:1991-8178 EISSN: 2309-8414
Journal home page: www.ajbasweb.com



Biogasoline synthesis from rubber seed oil through thermal fluid catalytic cracking

^{1,2}Syaiful Nizam Hassan, ²Rafidah Farhana Sarulnisah, ²Mushtaq Ahmed, ²Abdul Aziz Abdul Raman, ²Nik Meriam Nik Sulaiman

¹Chemical Engineering Department, Faculty of Engineering, Universiti Malaya, 50603 Kuala Lumpur, Malaysia.

²Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Gambang, 26300 Kuantan, Pahang, Malaysia.

Address For Correspondence:

Syaiful Nizam Hassan. Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Gambang, 26300 Kuantan, Pahang, Malaysia.
Tel: +6095492820; E-mail: syaiful@ump.edu.my

ARTICLE INFO

Article history:

Received 18 September 2016

Accepted 21 January 2017

Available online 26 January 2017

Keywords:

Biogasoline; rubber seed oil; fluid catalytic cracking; cracking temperature; catalyst mass; gas chromatography

ABSTRACT

Biogasoline as a fuel has the same characteristics as that of commercial gasoline in terms of its molecular formula and physico-chemical properties. In this research, biogasoline was synthesized from rubber seed oil (RSO), which contains liquid forms of unsaturated fatty acids. Fluid catalytic cracking (FCC) process was selected and applied to convert RSO to biogasoline. Catalyst used for this conversion was ZSM-5 zeolite, and the apparatus used was the FCC equipment set. Design of experiment was performed using 4 parameters those are RSO mass, catalyst mass, cracking temperatures and cracking durations. RSO was heated and cracked; followed with the product condensation. The product was analyzed using gas chromatography method to analyze new-arranged gasoline-like hydrocarbon compounds in the liquid product. To synthesize and produce biogasoline from rubber seed oil through thermal FCC; and also to optimize applied cracking temperatures during rubber seed oil conversion to acceptable yield of biogasoline. The yield of biogasoline obtained was achieved at maximum 35% from 25.0 g RSO that was cracked at 350 °C, 1.0 g catalyst and 45 minutes, which was within 15% to 65% from various vegetable oils and other organic resources using FCC method. Those results shown that RSO was another potential source of biogasoline production through only FCC conversion method, and the research objectives were achieved.

INTRODUCTION

The rubber plant which is widely used as a natural source of rubber has been reported to have oil rich seeds (Njoku *et al.*, 1996). Although there are many variations in the oil content of the seed from different countries, the average oil yield have been reported to be 40% (Hilditch, 1951; Njoku *et al.*, 1996 and Ikwuagwu *et al.*, 2000). Rubber seeds were also reported about 43% oil content (Nwokolo *et al.*, 1988). Rubber tree starts to bear fruits at four years of age. In this research, rubber seed oil is selected as the starting material to be converted to biogasoline, which is the renewable gasoline-like fuel. Biogasoline should be synthesized based on two main reasons. First, the consumptions of both biodiesel and bioalcohols are currently limited although their productions have already succeeded, based on their current applications and feedstocks. Second, biogasoline synthesis is still not developed *yet* although there are various vegetable oils and recyclable organic materials those are reliable.

Open Access Journal

Published BY AENSI Publication

© 2017 AENSI Publisher All rights reserved

This work is licensed under the Creative Commons Attribution International License (CC BY).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

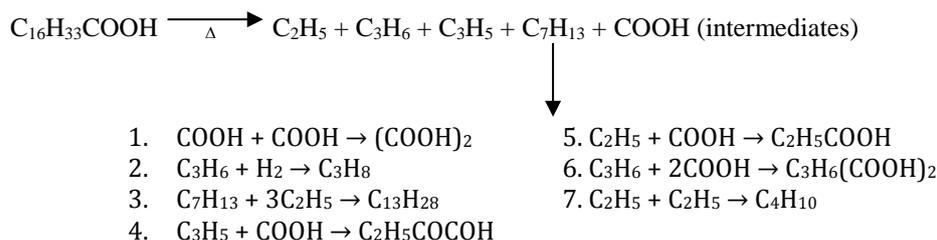
To Cite This Article: Syaiful Nizam Hassan, Rafidah Farhana Sarulnisah, Mushtaq Ahmed, Abdul Aziz Abdul Raman, Nik Meriam Nik Sulaiman., Biogasoline synthesis from rubber seed oil through thermal fluid catalytic cracking. *Aust. J. Basic & Appl. Sci.*, 11(3): 104-113, 2017

Biogasoline is generally synthesized from vegetable oils and other biomass sources, so it is biodegradable, non-toxic and environmental-friendly, regarding from the environmental point of view for fuels from vegetable sources. Since its properties had been determined and investigated similar with commercial gasoline, so the biogasoline synthesis was continued and well-established (Bruno, 2011). Biogasoline is able to suppress certain pollutants that come up from the exhaust, with the exception of NO_x in certain cases, where unpredictable results occurred. Biogasoline or gasoline-like biofuel characteristics stated in previous research articles are same with gasoline after distillation at gasoline's boiling temperature range (40 °C – 205 °C) and analysis using standard gasoline's API and ASTM methods of the cracked biofuel feedstock. Previous researchers have found that biogasoline had already synthesized by various vegetable oils through FCC method. However, the inedible vegetable oils and the used vegetable oils had already preferred for biogasoline syntheses to minimize negative-impact competition with food consumption by using edible crude vegetable oils (Demirbas, 2009). The same researchers have predicted the satisfaction results of the biogasoline synthesized through vegetable oil conversions during performing experiments run by them, which have exceeded 40% w/w from vegetable oil feed (Demirbas, 2009; Lam *et al.*, 2011; Yean-Sang *et al.*, 2003; Chang and Wan, 1946). Biogasoline is also produced through FCC of biomass, and separated from other organic liquid products after the FCC is completed. Currently, the biogasoline has its own potential to be produced and commercialized; and it will compete the current commercialized bioalcohols. This is because biogasoline fulfills the qualitative standard specifications and characterizations of API and ASTM for commercial gasoline, as has been proved by Chang and Wan (1946), Benallal *et al.* (1994) and Demirbas (2008), as shown in Table 1.

Table 1: Properties of waste engine oil biogasoline and commercial gasoline (Cited: Demirbas, 2008)

Property	Waste engine oil biogasoline	Commercial gasoline	Test
Octane number	96	89	ASTM D 2699
Density at 288 K (kg/m ³)	0.732	0.735	ASTM D 1298
Sulphur content (% w/w)	0.003	0.002	ASTM D 1266
Higher heating value (MJ/kg)	45.9	47.8	ASTM D 2015
Flash point (K)	245	249	
Dynamic viscosity at 300 K mm ² /s)	1.13	1.17	
Colour	Yellow	Yellow	
Initial boiling point (K)	304	312	
End point (K)	445	454	

FCC is defined as cracking fluid substances in closed vessel at suitable temperatures to obtain lighter substances using direct heating, with presence of catalyst and inert gas as carrier fluid (Demirbas *et al.*, 2009). Fluid catalytic cracking is a well-established refinery processes for production of light hydrocarbon compounds from heavy hydrocarbon feedstock (Bielansky *et al.*, 2011). Additionally, this cracking leads to perform isomerization, and the catalyst used for this process is the heterogeneous solid type that also plays its work of separating branched molecules and straight molecules (Suhaimi and Halim, 2010). In this research, during this cracking process of the oil, the long-chain triglycerides were broken either one or more places in every single chain. For example, palmitic acid (C₁₆H₃₃COOH) could be broken in more than one possibilities as follows:



In FCC, various parameters such as cracking temperature, cracking duration period, feed velocity (in weight hourly space velocity (WHSV)), feed flow rate, feed pressure, feed viscosity, dimensions of cracker chamber (length, cross-sectional area, volume and size), typical catalyst used, dimensional properties of catalyst (mesh size, surface area, voids and bulk capacity), product flow rate and product viscosity were applied in order to achieve the satisfied-resulting conversions of vegetable oils to desirable biofuel products. The rate of cracking is dependent on the temperature and pressure applied as well as the presence of the catalyst. Temperature, heating rate, residence time and type of catalyst choice are important process control parameters (Ni *et al.*, 2006). The success of FCC of various vegetable oils to produce various types of biofuels (except biodiesel and focused to biogasoline) until that process have been already well-established is proved by experimental works (Amin, 2006; Bielansky, 2011; Bhatia, 2011). After the FCC process was confirmed for biogasoline synthesis and production, the catalytic cracking parameters should be optimized in order to maintain (or increase) biogasoline

yield. Optimization studies of certain parameters during vegetable oil conversion to biogasoline and other biofuels (except biodiesel) were also performed. For example, palm oil was 95% w/w converted, with 80% w/w feed was organic liquid product and 50% w/w feed was biogasoline. All those presented conversion results had been achieved after 3 parameters of cracking temperature, catalyst to oil ratio and cracking residence time were optimized at 450 °C, 5.00 g/g and 20 s respectively (Bhatia, 2006).

In modern catalytic cracking applications, zeolites are used as catalysts instead of using oxides of transition metals in previous catalytic cracking (Twaiq *et al.*, 2001 – 2004). Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves", those refer to a particular property of these materials, which is the ability to select sort molecules primarily based on a size exclusion process, due to a very regular pore structure of molecular dimensions. They are commonly commercialized and applied as adsorbents. Since 1989, there have been several other studies on the production of hydrocarbons from palm oil mainly biogasoline (Bhatia *et al.*, 2003 - 2007) which have been carried out using cracking catalysts in a micro-reactor. Zeolites have shown excellent performance as solid acid cracking catalysts due to their higher selectivity (Twaiq, 2001 – 2004). Since zeolites are extremely active, therefore it has been tested extensively for catalytic cracking, especially of vegetable oil (Yean Sang, 2003; Tamunaidu, 2007 and Bhatia *et al.*, 2003 – 2007). For zeolite selection, zeolite ZSM-5 was selected as the best catalyst for fluid catalytic cracking of liquid crude organic compounds, either petroleum (Degnan, 1999) or fluid lipids (vegetable oils and fats). This is because the performances of original ZSM-5 is better than original MCM-41 (Kim & Kim, 2008), ZSM-11 (Xu, 2009) and original USY (Adewuyi, 1995). Furthermore, most researchers preferred ZSM-5 as catalyst during converting vegetable oils and fats to biogasoline and other organic fluid compounds (Adewuyi, 1995; Buchanan, 1995, 1998 & 2001; Bao, 2007; Xu, 2009; Kim & Kim, 2008; Makkee, 2001; Corma, 2007 and Baranak, 2013). The ZSM-5's Si/Al ratio of 50:1 upgrades its catalytic reactivity performance (Wan Daud, 2011), especially for biogasoline conversion. This is because according to different ratios of Si/Al, gasoline product decreased when the Si/Al ratio increased (Buchanan, 1998).

The objectives of this research are to synthesize and produce biogasoline from rubber seed oil through thermal FCC, and also to optimize applied cracking temperatures during rubber seed oil conversion to acceptable yield of biogasoline.

MATERIALS AND METHODS

Apparatuses used in this research were the stirring-heating mantle, single-neck spherical flask, dean stark, glass condenser connected with water-cooling chiller, sampling vials, weighing machine, weighing boats for weighing catalyst, heat-resisting gloves, metal stirrer bars, big-sized retort stand, laboratory clippers, clipper-tiers and filter. Chemical substances used were rubber seed oil as the main reagent (after being extracted from rubber seed kernels those was purchased from USE Technology Supplies Sdn. Bhd.), zeolite ZSM-5 as the catalyst that was purchased from Zeolyst International Co. Ltd. (U.S.A.); and two standard substances as controls for analysis, which were artificial gasoline mixtures of C5 to C12 components those purchased from Orbital Scientific Technologies Sdn. Bhd.; and commercial gasoline that was purchased from Shell petrol station. 5 variables were considered in this fluid catalytic cracking process, which were cracking temperatures, cracking pressures (if co-reactant gas inlet involves in reaction), cracking durations, masses of catalyst and feed flow rates, depended on typical fatty acid components (Bhatia op cit, 2006).

Table 2 demonstrated the design of experiment (DOE) that was finalized after using Design Expert software through Taguchi method that monitored the fittest reaction conditions, those were 9 experiment runs from 80 experiment runs of manual DOE settings, simultaneously with Design Expert simulation. This DOE finalization regarding all 4 parameter inputs, due to the analysis of variance of the expecting experiments and resulting products at following 2nd set-up FCC conditions (623 K (350 °C) – 723 K (450 °C), 30 min – 45 min, 0.5 g – 1.5 g catalyst, 24.5 g - 25.5 g rubber seed oil). In this research, rubber seed oil mass was fixed and cracking pressure parameter was not included. This was because no additional gases had involved and taken part in this reaction. Previous literatures also described that the FCC only involved the single reactant (either vegetable oil or waste organic oil) only. Figure 1 presents the experiment set-up. In this set-up, the spherical flask (already filled with metal stirrer bar, rubber seed oil and catalyst) was put inside the stirring-heating mantle, and firstly connected with dean stark. The dean stark was then clipped with a laboratory clipper, tied with clipper tiers to big-sized retort stand and positioned vertically. The condenser was then attached together with dean stark using other two laboratory clippers paired with clipper-tiers at the same retort stand. The flask was then covered with aluminum foil to minimize losses of heat from mantle and vapour from reacted flask contents to surroundings. For safety, the set-up was arranged inside the fume hood and the hood was operated for safe ventilation. Finally, the heating mantle was switched on with fixed 4000 rpm stirring speed for all runs and temperature setting as scheduled. After the completion of both cracking and condensation processes for each experiment run, the product (in liquid-phase form) was discarded into sample-collecting vials. The sample-collecting vials with the filled liquid product were then brought for analysis.



Fig. 1: Experimental set-up of RSO FCC.

Table 2: Tabulated DOE of RSO FCC after being finalized using Design Expert.

Run of experiment	Parameters			
	T (°C)	m_{oil} (g)	$m_{catalyst}$ (g)	t (min)
1	350	25	0.5	30
2			1.0	45
3			1.5	60
4	400		0.5	45
5			1.0	60
6			1.5	30
7	450		0.5	60
8			1.0	30
9			1.5	45

All product samples obtained were sipped out of 5 μ l each using a 1- μ l – 100- μ l micro-pipette. Then the sipped sample was mixed well with 1.5 ml GC-grade n-pentane solvent inside 1.5-ml sample-analysis vial. After the mixing of sample-solvent process was completed, each sample-analysis vial was brought to Agilent Gas Chromatographer with conditions listed in Table 3. To investigate that the product contained desired biogasoline or not through GC method, the calibration standards should be prepared. In this study so far, only n-hexane, n-heptane, 2,2,4-trimethylpentane (isooctane), cyclohexane, benzene and methylbenzene (toluene) were available. The standard calibration graphs of all 6 individual gasoline components (n-hexane, n-heptane, isooctane, cyclohexane, benzene and toluene) had already prepared, with their linear equations as follows:

$$\text{n-hexane} \quad : y = 3.6308x - 88.713 \quad (\text{Equation 1})$$

$$\text{n-heptane} \quad : y = 3.7154x - 80.906 \quad (\text{Equation 2})$$

$$\text{isooctane} \quad : y = 6.1927x - 55.2 \quad (\text{Equation 3})$$

$$\text{cyclohexane} : y = 12.233x - 469.2 \quad (\text{Equation 4})$$

$$\text{benzene} \quad : y = 3.9542x - 59.285 \quad (\text{Equation 5})$$

$$\text{toluene} \quad : y = 10.871x - 263.32 \quad (\text{Equation 6})$$

with y = chromatogram peak area of the standard individual hydrocarbon component in pA*s and x = hydrocarbon component concentration in ppm. Next, all the obtained concentration values were totalized together to determine the percentages of both represented biogasoline fraction (in the product) and yield (from the rubber seed oil before conversion) of the entire sample, as shown in Equations 7 and 8 as follows:

$$\frac{\text{Gasoline content (ppm)} * 100}{[(0.005 \text{ ml} * 1000)/1.5 \text{ ml mix}]} = \text{Gasoline fraction (\%)} \quad (\text{Equation 7})$$

$$\frac{\text{Gasoline content (g)} * 100}{\text{Rubber seed oil (g)}} = (\text{Bio})\text{gasoline yield (\%)} \quad (\text{Equation 8})$$

Table 3: Listed conditions set-up of Agilent GC for biogasoline analysis.

Sampling preparations		5.0 μ l sample in 1.5 ml GC-grade C_3H_{12} solvent
	Inlet	280 °C
	Initial	30 °C

GC temperature set	Final	150 °C
	Detector	180 °C
Heating rate	20 °C/min	
GC runtime	Equilibrium	0.5 min (30 seconds)
	Total	9.0 min

RESULTS AND DISCUSSION

From all experiment runs performed, it was shown that the product from the cracked rubber seed oil was formed in two or three immiscible layers after condensation inside the dean stark. Both layers were discarded separately using 2 sample-collecting vials and labelled. The golden colour of the top layer represented the short-chain fatty acids, whereas the clear bottom layer represented the liquid hydrocarbon substance that hypothetically considered as saturated hydrocarbons. This is because during the cracking process, the long-chain triglycerides were broken either one or more places in every single chain.

Tables 4 and 5 represented the overall results of rubber seed oil conversion, biogasoline fractions in cracked RSO product and biogasoline yield in 25.0 g rubber seed oil, based on the mass and percentage calculations. Whereas Figures 2 until 4 showed the graphical curves of the biogasoline yield that was measured in mass affected from each condition parameter, those were already referred from Table 5. Both latter results were obtained from biogasoline concentration results from GC calibration data gas chromatograms of several individual gasoline component standards using Equations 1 to 7.

Table 4: Overall results of RSO conversion to biogasoline

Experiment run		1	2	3	4	5	6	7	8	9
Mass (g)	Converted RSO	19.90	21.51	16.44	11.12	22.99	16.17	20.26	18.70	22.13
	Liquid product	11.66	11.45	7.65	8.61	8.05	14.46	8.09	12.01	15.58
	Gasoline yield in RSO	0.39	8.72	3.47	0.20	4.69	2.37	4.47	4.40	0.39
Percent (%)	Converted RSO	79.60	86.04	65.76	44.48	91.96	64.68	81.04	74.80	88.52
	Liquid product	46.64	45.80	30.60	34.44	32.20	57.84	32.36	48.04	62.32
	Gasoline yield in RSO	1.57	34.86	13.88	0.79	18.76	9.49	17.87	17.61	1.57

Table 5: Masses of biogasoline yield from cracked 25 g rubber seed oil through fluid catalytic cracking.

Experiment run	Cracking temperature (°C)	Catalyst loading (% wt)	Cracking period (min)	Gasoline yield (%)	Gasoline yield mass (g)
1	350	2	30	1.57	0.39
2	350	4	45	34.86	8.72
3	350	6	60	13.88	3.47
4	400	2	45	0.79	0.20
5	400	4	60	18.76	4.69
6	400	6	30	9.49	2.37
7	450	2	60	17.87	4.47
8	450	4	30	17.61	4.40
9	450	6	45	1.57	0.39

The differences between the converted rubber seed oil and the total liquid product showed that the rest of the rubber seed oil was transformed into biogas during the conversion. This was because during cracking process, the long-chain triglyceride molecules were randomly broken by supplied heat from heating mantle. All these molecules broke into various smaller molecules those form firstly in vapour, and during entering the condenser that operated below 5 °C, the vapour partially condensed into liquid form. Generally, the C1 to C4 molecules produced were considered as gas, whereas the rest (from C5 to C15) molecules produced were considered as liquid. This was because at atmospheric pressure, the boiling points of gaseous C1 to C4 molecules were -162 °C, -89 °C, -42 °C and 0 °C respectively; whereas the boiling points of the rest molecules were between 36 °C to 250 °C.

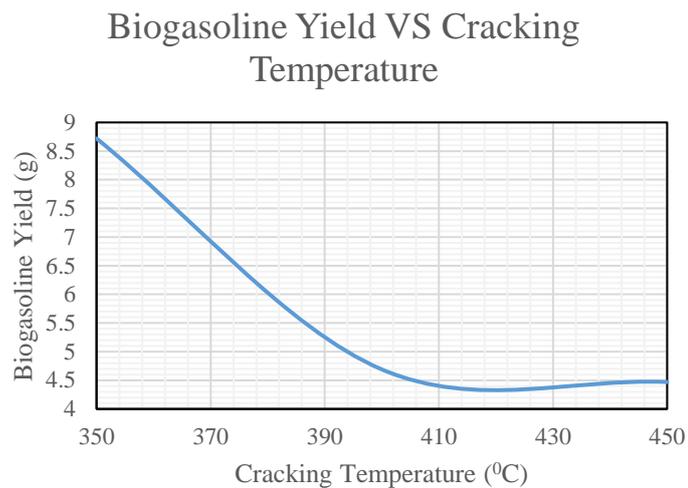


Fig. 2: Graph of measured biogasoline yield affected by cracking temperatures.

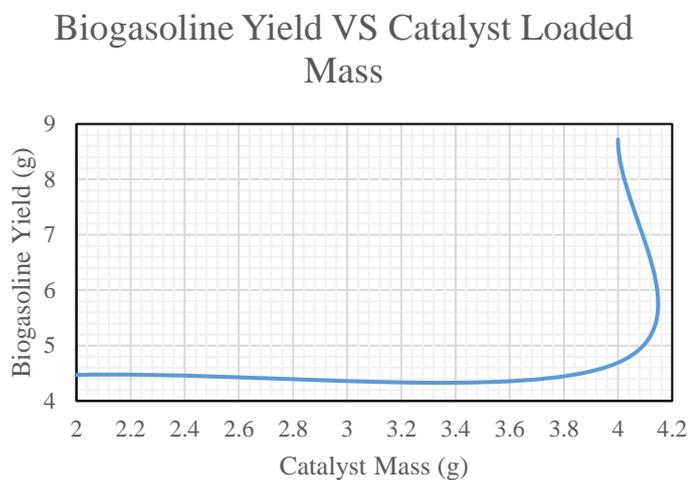


Fig. 3: Graph of measured biogasoline yield affected by catalyst masses.

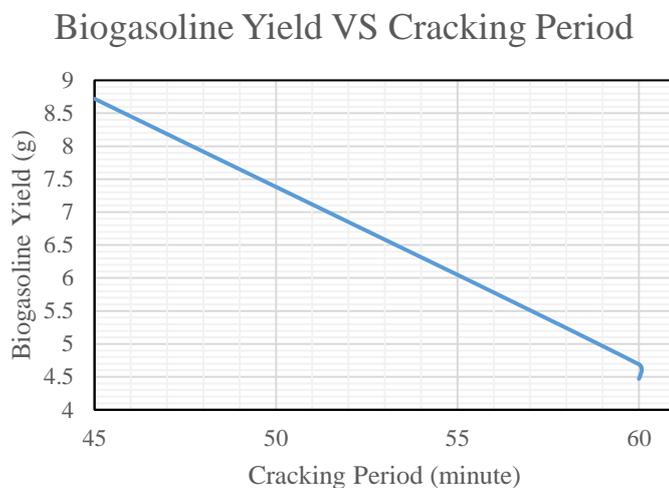


Fig. 4: Graph of measured biogasoline yield affected by cracking periods.

The stirring process during heating rubber seed oil advanced all 3 conversion mechanisms. This was because the stirred zeolite particles led to provide maximum reaction surfaces and voids for hydrocarbon radicals' attachment in order to enhance both recombination and isomerization among new smaller radical forms those occurred simultaneously with cracking triglycerides, so zeolite could play its role during both processes. Generally, the recombination occurred first, following by isomerization. In recombination process, all the cracked molecules were recombined into mixtures of smaller hydrocarbons, either linear form (for example hexane, heptane, octane etcetera) or cyclic (for example cyclohexane) or aromatics (for example benzene and toluene). Consequently in isomerization, the rest of radicals attached the incomplete recombined main hydrocarbon molecules to produced isomerized molecules (for example isoctane and xylenes).

Table 6 represented the effects of both temperature and catalyst mass set-up for each experiment run on rubber seed oil conversion, liquid product condensate formed and biogasoline yield obtained. From Table 5, at 350 °C, all results obtained were high. It was meant that at that temperature the rubber seed oil was 86.04% converted, followed by 45.8% liquid product condensed from that cracking process and finally the biogasoline yielded was 34.86%. This was affected also from 1.0 g catalyst and 45 minutes of cracking duration. For 400 °C, although the rubber seed oil was 91.96% converted, the biogasoline yield was lower than 350 °C, which was 18.76%. This was because the yield was affected by the lower percentage of liquid product condensed (32.20%), and the longer cracking duration (60 minutes) that converted more to biogas. Finally at 450 °C, all biogasoline yields were lower than the previous presented. This was because although the rubber seed oil were highly converted at that temperature, and obtaining the highest liquid product condensate (62.32%), the high temperature also could reduce zeolite's reactivity because of the lowering its reaction surface.

Table 6: Effect of temperature to the RSO conversion and biogasoline yield.

Run	Temperature in °C	Other parameters	Result obtained in %		
			Converted RSO	Liquid product	Gasoline yield in RSO
1	350	0.5 g, 30 min	79.60	46.64	1.57
2		1.0 g, 45 min	86.04	45.80	34.86
3		1.5 g, 60 min	65.76	30.60	13.88
4	400	0.5 g, 45 min	44.48	34.44	0.79
5		1.0 g, 60 min	91.96	32.20	18.76
6		1.5 g, 30 min	64.68	57.84	9.49
7	450	0.5 g, 60 min	81.04	32.36	17.87
8		1.0 g, 30 min	74.80	40.84	17.61
9		1.5 g, 45 min	88.52	62.32	1.57

Table 7 represented the effects of catalyst mass set-up for each experiment run on rubber seed oil conversion, liquid product condensate formed and biogasoline yield obtained. From Table 6, 1.0 g catalyst used showed the highest yields of biogasoline in RSO, which were between 17.61% - 34.86%. Whereas both 0.5 g and 1.5 g catalyst used showed lower yields those were between 0.79% - 17.87%. Table 6 also showed that RSO conversion was only obviously affected by the masses of catalyst used. The liquid product obtained did not fully follow the RSO conversion because the conversion itself produced various multi-phase products. However, it was agreed that low conversion resulted lower yields, especially for 1.5 g catalyst used. This was occurred from the opening spaces between the catalyst particles, the reaction surface and voids among the catalyst, and the limitation of heat supply, period and space of recombining and isomerizing cracked molecules.

Table 7: Effect of catalyst mass to the RSO conversion and biogasoline yield.

Run	Catalyst mass in g	Other parameters	Result obtained in %		
			Converted RSO	Liquid product	Gasoline yield in RSO
1	0.5	350 °C, 30 min	79.60	46.64	1.57
4		400 °C, 45 min	44.48	34.44	0.79
7		450 °C, 60 min	81.04	32.36	17.87
2	1.0	350 °C, 45 min	86.04	45.80	34.86
5		400 °C, 60 min	91.96	32.20	18.76
8		450 °C, 30 min	74.80	40.84	17.61
3	1.5	350 °C, 60 min	65.76	30.60	13.88
6		400 °C, 30 min	64.68	57.84	9.49
9		450 °C, 45 min	88.52	62.32	1.57

Table 8 represented the effects of cracking duration set-up for each experiment run on rubber seed oil conversion, liquid product condensate formed and biogasoline yield obtained. From Table 7, the highest yield of biogasoline in RSO, which was 34.86%, had been achieved after 45 minutes RSO conversion, together with 1.0 g catalyst used at 350 °C. Whereas all experiments those were run in 30 minutes only obtain lowest yields those were within range 1.57 % - 17.61 %. It was shown that the shorter cracking duration was not enough to crack RSO at maximum amount, whereas the longer cracking duration would increase the gaseous products of that conversion. This was because both liquid product and biogasoline yield obtained were lower for 60 minutes

cracking than for 45 minutes cracking. However, in overall, all those parameters affected the overall results obtained in different ways, so the overall results obtained were not parallel.

Table 8: Effect of cracking duration to the RSO conversion and biogasoline yield.

Run	Cracking duration in minutes	Other parameters	Result obtained in %		
			Converted RSO	Liquid product	Gasoline yield in RSO
1	30	0.5 g, 350 °C	79.60	46.64	1.57
8		1.0 g, 450 °C	74.80	40.84	17.61
6		1.5 g, 400 °C	64.68	57.84	9.49
2	45	0.5 g, 400 °C	44.48	34.44	0.79
4		1.0 g, 350 °C	86.04	45.80	34.86
9		1.5 g, 450 °C	88.52	62.32	1.57
3	60	0.5 g, 450 °C	81.04	32.36	17.87
5		1.0 g, 400 °C	91.96	32.20	18.76
7		1.5 g, 350 °C	65.76	30.60	13.88

When comparing all results shown in Tables 6, 7 and 8 with the results from previous related researches, it was shown that the biogasoline yield resulted from catalytic-cracked rubber seed oil was within the range of 16% to 65% from conversion of all kinds of organic resources. This was because all previous researches also used the temperature range 150 °C – 600 °C in order to ensure the success of vegetable oils' conversions to biogasoline through fluid catalytic cracking is achieved. Three examples proved this evidence. As first example, the palm oil was converted 80% - 96% w/w from palm oil feed and selective-yielded 16% - 35% w/w biogasoline from palm oil at 500 °C, 2.5 h⁻¹ WHSV and 1 atm with Cu-ZSM-5 catalyst for 4 hours (Amin, 2006). Second example, mixture of both oleic and palmitic acids were converted into maximum 44% w/w yields of biogasoline after running similar process at 485 °C – 550 °C, 1 l/h – 3 l/h feed flow rate, 1.0 s – 1.6 s residence time and ambient pressure using pilot-plant-scaled fluid catalytic cracker, 250 °C – 320 °C pre-heated feed combined with inert gas and 9 kg – 11 kg of 79 µm-diameter pre-heated REUSY-ZSM-5 zeolite catalyst (Bielansky, 2012). Third example, fluid catalytic cracking of waste cooking palm oil with 86.4% conversion (at parameters: 458 °C, 2.5 h⁻¹ WHSV, 1 atm, oil to catalyst ratio 6:1 (w/w), catalyst pore size 0.67 nm); 90.8% conversion (at parameters: 450 °C, 2.5 h⁻¹ WHSV, 1 atm, oil to catalyst ratio 6:1 (w/w), catalyst pore size 0.54 nm) and 92.0% conversion (at parameters: 500 °C, 2.5 h⁻¹ WHSV, 1 atm, oil to catalyst ratio 10:1 (w/w), catalyst pore size 0.54 nm) yielded 33.5%, 36.4% and 35.5% w/w gasoline respectively (Bhatia, 2011).

From the prepared calibration standards of n-hexane, n-heptane, 2,2,4-trimethylpentane, cyclohexane, benzene and toluene, the retention time range and retention time average obtained for each component was listed as shown in Table 9. However, the average retention time stated was only the approximation; the main priority was the retention time range itself. From Table 9, it could be considered that, all the components between 0.8 – 1.1 minute were considered as biogasoline. Whereas all the components below 0.8 minute were considered as biogas and all the components those exceed 1.1 minute were considered as biodiesel.

Table 9: List of retention time range for each calibration HC component

Standard calibration component	Retention time range (minutes)	Average retention time (minutes)
n-hexane	0.817 – 0.828	0.8209
n-heptane	0.920 – 0.926	0.9215
2,2,4-trimethylpentane	0.892 – 0.921	0.9043
Cyclohexane	0.872 – 0.879	0.8751
Benzene	0.872 – 0.881	0.8773
Methylbenzene (toluene)	1.081 – 1.102	1.0895
Overall	0.817 – 1.102	0.8209 – 1.0895

After analyzing all samples' chromatograms with reference of all standards' chromatograms, it was found that all samples had at least one gasoline component present. By matching individual components' peak areas with their own retention times (in chromatograms) and then with concentration (in standard calibration graphs), the concentration for each component could be determined. Using Microsoft Excel program in automatic-calculation mode for each standard calibration graph, each gasoline component's concentration (in ppm) would be automatically determined by inserting its peak area value. During running gas chromatography analysis, only 6 hydrocarbon chemicals were available for standard calibration. Several additional hydrocarbon chemicals were still not available, so the gasoline determination could not be declared yet. According to previous analyses of commercial gasoline, there were totally mixtures of 25 components in all gasoline samples analyzed, which consisting paraffins as major component category, together with olefins, aromatics and oxygenates.

According to the standard procedure of GC analysis method on fluid organic samples, the quantity of sample taken for GC analysis was very small (5.0 µl mixed with 1500.0 µl GC-grade n-pentane), and then followed with 1.0 µl mixture injected into GC column, the possibilities of the resulting yield differentiation could occur. For 1st example, the 3rd experiment run (25.0 g RSO, 1.0 g catalyst, 350 °C, 45 minutes of

cracking) yielded 34.86%, but this yield would change if the same sample was reanalyzed 2nd time onwards with lower yields, either slight lower or far lower than 34.86%. This was because the cracked molecules moved randomly and independently in the “huge space” among n-pentane molecules, so not all the cracked molecules were sipped and injected together. Generally, the yield resulted directly correlated with the amount of sipped and injected cracked molecules during overall GC analysis.

Conclusions:

From the results of biogasoline yield obtained, it was concluded that the highest biogasoline yield from rubber seed oil through FCC was 34.86% w/w at 350 °C, 1.0 g zeolite ZSM-5 catalyst used for 45 minutes processing for 25.0 g rubber seed oil. From all experiment runs, 50% experiments obtained the biogasoline yields those fit 16% - 69% w/w range of biogasoline yields stated in literature. Finally, the objectives of this research study were successfully achieved and should be continued together with other biogasoline resources using FCC only.

ACKNOWLEDGEMENTS

Special thanks firstly to both my supervisors Prof. Ir. Dr. Abdul Aziz bin Abdul Raman and Prof. Dr. Nik Meriam binti Nik Sulaiman whom directly conduct together with me for my research study; secondly to Yahya Muhammad Sani, Mushtaq Ahmed, Rafidah Farhana binti Sarulnisah and all technical staffs from Chemical Engineering Department, Engineering Faculty, University of Malaya whom assisting me during my research activities; thirdly to Prof. Dr. Abdurrahman Hamid Nour from Chemical Engineering Faculty, University Malaysia Pahang; fourthly to committees of Study Leave Unit of Human Resources, also in University Malaysia Pahang those having given me an opportunity to continue Ph.D. study in University of Malaya, and finally to Elsevier Science Ltd. that publishing both my ISI journal papers as graduation condition for my research study.

REFERENCES

- Adewuyi, Y.G., J.S. Buchanan and D.J. Klocke, 1995. Effects of high-level additions of ZSM-5 to a fluid catalytic cracking (FCC) RE_USY catalyst, *Applied Catalysis A: General* Vol 131, Elsevier Science Ltd., pp: 121-133.
- Amin, N.A.S. and T.B. Siregar, 2006. *Catalytic Cracking of Palm Oil to Gasoline Over Pre-treated Cu-ZSM-5*, *Jurnal Teknologi* Vol. 44(F), Jun 2006, Universiti Teknologi Malaysia, pp: 69-82.
- Bao, X., Y. Fan, X. Lin, H. Liu, Z. Liu and G. Shi, 2007. A novel method for enhancing on-stream stability of fluid catalytic cracking (FCC) gasoline hydro-upgrading catalyst: Post-treatment of HZSM-5 zeolite by combined steaming and citric acid leaching, *Catalysis Today*, 125, Elsevier Science Ltd., pp: 185-191.
- Baranak, M., B. Guranlu, A. Sarioglan, O. Atac and H. Atakul, 2012. Low Acidity ZSM-5 supported iron catalysts for Fischer-Tropsch synthesis, *Catalysis Today* Vol 207, Elsevier Science Ltd., pp: 57-64.
- Benallal, B., C. Roy, H. Pakdel, S. Chabot and M.A. Poirier, 1994. Characterization of Pyrolytic Light Naphtha from Vacuum Pyrolysis of Used Tyres – Comparison with Petroleum Light Naphtha, *Fuel*, 74(11): 1589-1594.
- Bhatia, S. and P. Tamunaidu, 2006. Catalytic cracking of palm oil for the production of biofuels – optimization studies, *Bioresource Technology*, Elsevier Science Ltd., 28: 3593-3601.
- Bhatia, S., A.R. Mohamed and N. Taufiqurrahmi, 2011. Production of Biofuel from Waste Cooking Palm Oil using Nanocrystalline Zeolite as Catalyst: Process Optimization Studies, *Bioresource Technology*, 102: 10686-10694.
- Bielansky, P., A. Weinert, C. Schonberger and A. Reichhold, 2011. Gasoline and gaseous hydrocarbons from fatty acids via catalytic cracking, *Biomass Conversion and Biorefinery*, 1(3): 1-9.
- Bruno, T.J. and G. Anitescu, 2011. Liquid Biofuels: Fluid Properties to Optimize Feedstock Selection, Processing, Refining/Blending, Storage/Transportation, and Combustion, *Energy and Fuels*, 26, ACS Publications, 324-348.
- Buchanan, J.S., 1998. Gasoline selective ZSM-5 FCC additives: Model reactions of C6-C10 olefins over steamed 55:1 and 450:1 ZSM-5, *Applied Catalysis A: General*, 171: 57-64.
- Buchanan, J.S. and Y.G.A dewuyi, 1995. Effects of high temperature and high ZSM-5 additive level on FCC olefins yields and gasoline composition, *Applied Catalysis A: General.*, 134: 247-262.
- Buchanan, J.S., D.H. Olson and S.E. Schramm, 2001. Gasoline selective ZSM-5 FCC additives; effects of crystal size, SiO₂/Al₂O₃, steaming, and other treatments on ZSM-5 diffusivity and selectivity in cracking of hexane/octane feed, *Applied Catalysis A: General.*, 220: 223-234.
- Chang, C.C. and S.W. Wan, 1946. China's Motor Fuels from Tung Oil, *Industrial and Engineering Chemistry*, 39(12): 543-1548.

Corma, A., G.W.H. Uber, L. Sauvanaud and P. O'Connor, 2007. Processing Biomass Derived Oxygenates In The Oil Refinery: Catalytic Cracking (FCC) Reaction Pathways and Role of Catalyst. *Journal of Catalysis*, 247: 307-327.

Cvengros, J., E. Buzetzi, A. Kaszonyi, Z. Cvengrosova and K. Sidorova, 2011. The Influence of Zeolite Catalysts on the Products of Rapeseed Oil Cracking, *Fuel Processing Technology*, 92: 1623-1631.

Degnan, T.F., G.K. Chitnis and P.H. Schipper, 1999. History of ZSM-5 fluid catalytic cracking additive development at Mobil, *Microporous and Mesoporous Materials*, 35-36: 245-252.

Demirbas, A., 2008. Gasoline-like Fuel from Waste Engine Oil via Catalytic Pyrolysis, *Energy Sources Part A*, Taylor and Francis Group Publication, 30: 1433-1441.

Demirbas, A., 2009. *Biofuels*, Springer Press.

Halim, A.A.A., S.N. Hassan and M.A. Suhaimi, 2010. Concentration Of Biopetrol Synthesized From Palmitic Acid Through Catalytic Cracking Using Zeolite As Catalyst, *World Engineering Congress 2010 Proceedings*.

Hilditch, T.P., 1951. Variations in The Composition of Some Linolenic-Rich Seed Oils, *Journal of The Science Food and Agriculture*, 2(12): 543-547.

Ikwuagwu, O.E., O.U. Njoku and I.C. Ononogbu, 2000. Production of biodiesel using rubber [*Hevea brasiliensis* (Kunth. Muell.)] seed oil, *Industrial Crops and Products – An International Journal*, 12: 57-62.

Kim, J., S. Kim, S.K. Kim and T. Ngo, 2008. Pyrolysis of soybean oil with HZSM-5 (Proton exchange of Zeolite Socony Mobil 35) and MCM41 (Mobil Composition of Matter No. 41) catalysts in a fixed-bed reactor, *Energy*, 35: 2723-2728.

Lam, S.S., A.D. Russell, C.L. Lee, H.A. Chase, 2011. Microwave-heated Pyrolysis of Waste Automotive Engine Oil: Influence of Operation Parameters on Yield, Composition & Fuel Properties of Pyrolysis Oil, *Fuel*, 92: 327-339.

Makkee, M., M.A. Hollander, J.A. Mouljin and M. Wissink, 2001. Gasoline conversion: reactivity towards cracking with equilibrated FCC and ZSM-5 catalysts, *Applied Catalysis A: General*, 223: 85-102.

Nam, L.T.H., T.Q. Vinh, N.T.T. Loan, V.D.S. Tho, X.-Y. Yang and B.-L. Su, 2011. Preparation of bio-fuels by catalytic cracking reaction of vegetable oil sludge, *Elsevier Journal of Fuel*, 90(3): 1069-1075.

Ni, M., D.Y.C. Leung, M.K.H. Leung, K. Sumathy, 2006. An overview of hydrogen production from biomass. *Fuel Processing Technology Vol. 87*, Elsevier Science Ltd., pp: 461-472.

Njoku, O.U., I.C. Ononogbu, J.Y. Owusu, 1996. An investigation of oil of rubber (*Hevea brasiliensis*). *Journal of Rubber Research Institute of Sri Lanka*, 78: 52-59.

Nwokolo, E., D.D. Kills and J. Kanhoi, 1988. Serum and liver lipids of rats feed rubber seed oil. *Plant foods for Human Nutrition*, 38: 145-153.

Siriwardene, J.A. and D. Nugara, 1972. Metabolizable Energy of Rubber Seed Meal in Poultry Diets, *Ceylon Veterinary Journal*, 20(3): 61-63.

Tamunaidu, P. and S. Bhatia, 2007. Catalytic Cracking of Palm Oil For The Production of Biofuels: Optimization Studies. *Bioresource Technology*, 98: 3593-3601.

Twaiq, F.A., A.R. Mohamed and S. Bhatia, 2003. Liquid Hydrocarbon Fuels From Palm Oil By Catalytic Cracking Over Aluminosilicates Mesoporous Material With Various Si/Al Ratios. *Microporous Mesoporous Materials*, 64: 95-107.

Twaiq, F.A., N.A.M. Zabidi, A.R. Mohamed and S. Bhatia, 2003. Catalytic Conversion of Palm Oil Over Mesoporous Aluminosilicates MCM-41 For The Production of Liquid Hydrocarbon Fuels. *Fuel Processing Technology*, 84: 105-121.

Twaiq, F.A.A., N.A.M. Zabidi and S. Bhatia, 2001. Catalytic Cracking Of Palm Oil Over Zeolite Catalysts: Statistical Approach. *International Islamic University Malaysia Engineering Journal*, 2(1): 13-21.

Twaiq, F.A.A., A.R. Mohamad and S. Bhatia, 2004. Performance of Composite Catalysts In Palm Oil Cracking For The Production of Liquid Fuels And Chemicals. *Fuel Processing Technology*, 85: 1283-1300.

Wan Daud, W.M.A., J.N. Sahu and F. Abnisa, 2011. Optimization and characterization studies on bio-oil production from palm shell by pyrolysis using response surface methodology, *Biomass and Bioenergy*, 35: 3604-3616.

Xu, L., S. Xie, X. Li, Y. Wang, W. Xin, L. Zhang, H. Liu and S. Liu, 2009. Differences between ZSM-5 and ZSM-11 zeolite catalysts in 1-hexane aromatization and isomerization. *Fuel Processing Technology*, 91: 449-455.

Yean-Sang, O., F. Twaiq, R. Zakaria, A.R. Mohamed and S. Bhatia, 2003. Biofuel Production From Catalytic Cracking of Palm Oil. *Energy Sources*, 25(9): 859-869.