Light Liquid Fuel from Catalytic Cracking of Beef Tallow with ZSM-5

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Abstract- Beef tallow is a major waste from slaughterhouses and the production rate is rising due to increasing human population. Conversion of waste beef tallow into potential hydrocarbons and biofuels is of great interest. This work focused on catalytic cracking of beef tallow using ZSM-5 to generate a light liquid fuel. A batch reactor was used to investigate the effect of operating conditions for generation of liquid hydrocarbons using a central composite design of experiment to determine the maximum conversion. The experimental variables included reaction temperature between 350 and 450°C, reaction time from 20 to 60 min, and catalyst loading between 1.0 and 10.0% w/w. The liquid products obtained were subsequently distilled at 350°C and analyzed by gas chromatography–mass spectrometry for their chemical composition. The optimum condition for the highest liquid product conversion of 73% w/w was found at 443°C, 60 min and catalyst loading of 6.3% w/w. For the final light liquid fuel, different short chain hydrocarbons between C_7-C_{21} were identified. It contained mainly kerosene (36%), but with physical properties similar to diesel.

Keywords Animal fats; Biofuels; Catalytic upgrade; Renewable energy; Triglycerides.

1. Introduction

Energy is important and necessary in daily life. It is obvious that almost every activities are driven by energy. Moreover, energy is needed in order to develop our economy into the future. In Thailand, a 2014 report by the Thai Department of Alternative Energy Development and Efficiency, Ministry of Energy revealed that energy usage consisted of fossil fuels (75%(, large hydropower (14%), and other alternative energy .The proportion of renewable energy (10%) was rather low, consisting mainly of biomass (55%) solar (9%), and biogas (7%). This information may not come as a surprise since most countries still rely mostly on fossil fuels which are present with shortages and risk running out altogether. Use of fossil fuel is associated with pollutant gases which emit into the atmosphere [1] and are causative factors for the greenhouse effect and global warming. For all these reasons, it is critical that in the future, we prefer renewable energy sources to fossil fuels. Biofuel is advocated as an energy source that is amicable to the environment, specifically because of its carbon neutrality, low sulfur and nitrogen content [2].

Vegetable oil and animal fats are interesting choices as raw materials for biofuels [1-12]. In the northern part of Thailand, beef tallow is not popular as a food ingredient due to its malodorous quality. It may be studied for other potential uses. Tallow has many positive qualities such as being easy to find, transport and produce. But it has some characteristics that limit production, such as being a solid at room temperature and low energy density. In order to increase tallow quality to the level of existing fuels and to be competitive, tallow must be improved with regards to these aforementioned shortcomings [11, 12].

Upgrading the quality of tallow as a liquid fuel can be done by many ways. For instance, pyrolysis, high temperature cracking, renders tallow molecules and allows them to crack without a catalyst [13-15]. This method uses high temperature and pressure to destroy hydrocarbon bonds then reacts through free radical and carbonyl ionic mechanisms which produce a low volume, poor quality liquid fuel as compared to the catalytic cracking method. A core problem when dealing with pyrolysis oil is its higher water content and its instability because of the residence of organic compounds with unpleasing properties [15]. Next, the transesterification reaction changes triglycerides in tallow

to glycerol and esters through a chemical reaction using methanol as a solvent, which is a common way of producing biodiesel. The hydrocracking method employs hydrogen in order to eliminate of oxygen from the oil molecule out in the form of water, carbon dioxide, and carbon monoxide. This reaction relies on high pressure hydrogen and a high performance catalyst such as those in the transition metal class. Thus, this method has some limitations and high cost [16]. Alternatively, catalytic pyrolysis or catalytic cracking improves chemical structure by reducing energy consumption and increasing the reaction rate. Furthermore, this increases product quality to the level of the current process of petroleum fuels production. The triglycerides crack into fatty acids, which support the catalytic reaction and fatty acids will be converted to light products such as gasoline, light gases, and hydrocarbons. The main factor in this process is a catalyst that is developed with high selectivity, long life, increased productivity, and decreased production cost. It can be demonstrated that the catalytic cracking process provides many advantages in comparison to other processes [17-24].

Ong and Bhatia [17] presented a useful review on catalytic cracking of edible and non-edible oils. Mota et al. [18] reported large scale production of biofuels from catalytic cracking of palm oil using sodium carbonate as catalyst, with process yield over 65%. Da Silva Almeida et al. [19] was interested in generating organic light product from fats, oils and grease. Sodium carbonate was used in catalytic cracking. The product yield was around 60 to 67%. Twaiq et al. [20] studied cracking of palm oil and showed that conversion of palm oil using ZSM-5 catalyst with silica to alumina ratio of 50 produced high conversion (96.8 % w/w). Many studies described the use of ZSM-5 catalysts with great potential for conversion to highly aromatic gasolines, and very promising for conversion of triglycerides [21-23]. The role of ZSM-5 as an octane-boosting additive is due primarily to its shape selectivity. Shape selectivity effects are enhanced in addition to primary cracking. Thus, the increasing fractions of the olefins produced as intermediate products from primary cracking are aromatized to aromatic hydrocarbons [23].

In this research, catalytic cracking of beef tallow was investigated using ZSM-5 to generate a light liquid fuel in a batch reactor. Effect of operating conditions on product yield (reaction temperature between 350 and 450ºC, reaction time from 20 to 60 min, and catalyst loading between 1.0 and 10.0% w/w) was evaluated using a statistical design of experiment. Chemical and physical properties of the biofuel were also characterized.

2. Materials and Methods

2.1. Sample Preparation

Beef tallow from a slaughterhouse in Chiang Mai was used as the initial material. The beef tallow was prepared by washing and cleaning, then render at low temperature and finally filter dirty off. The beef tallow (Table 1) consists mainly of palmitic acid, stearic acid and oleic acid [24].

2.2. Catalyst

ZSM-5 is normally used in cracking process because of its high activity and stability, favorable selectivity. The ZSM-5 prepared by hydrothermal method was purchase from a commercial supplier. The catalyst characteristics are shown in Table 2. For activation, the catalyst was calcined at 550°C in the air for 4 h. Before being used, the catalyst was stored in a sealed vial in a desiccator to minimize the adsorption of the atmospheric moisture.

2.3. Experimental Setup

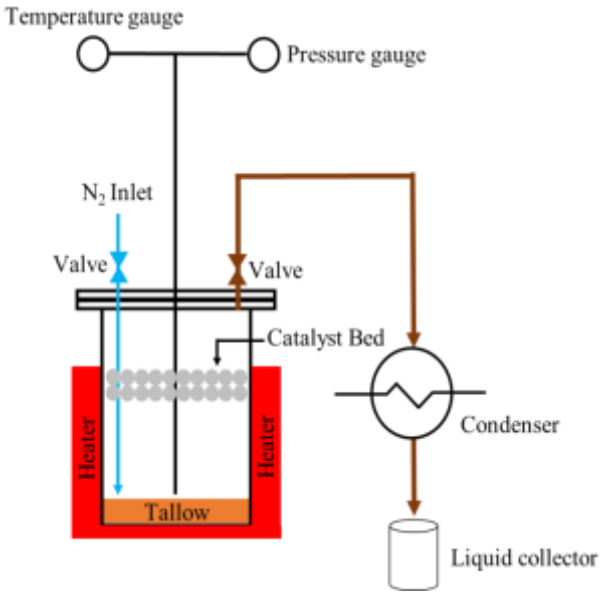
In this study, the catalytic cracking was carried out in a laboratory scale batch reactor. The reactor was made from stainless steel with 370 mm high, 10 mm thick and 152 mm in diameter. It was electrically heated and fully insulated. The temperature was controlled by a thermocouple inserted inside the reaction furnace. All catalytic cracking experiments were carried out under inert conditions with a cover sealed tight. Prior to each experiment, the air was purged from the reactor by nitrogen flow. Schematic diagram and picture of the batch reactor system is shown in Fig. 1.

Table 1. Typical fatty acid composition of beef tallow (% w/w), [24].

Saturated			**Unsaturated**				**Others**
myristic	palmitic	stearic	palmitoleic	oleic	linoleic	liolenic	
14:0	16:0	18:0	16:1	18:1	18:2	18:3	
3	26	14	3	47	3	1	3

Table 2. ZSM-5 characteristics.

Appearance	**Column (pelletized), solid**
SiO_2/Al_2O_3 molar ratio	38
Dimension	ø 2 mm, 2-10 mm long
Pore volume	≥ 0.25 cm^3/g
BET surface area	≥ 250 m^2/g
Bulk density	~ 0.72 kg/m^3
Crushing strength	≥ 98 N/cm^2
Attrition	< 1% w/w



(a)

(b)

Fig. 1. Schematic diagram and picture of reactor system.

2.4. Experimental Procedure

The schematic of cracking procedure is shown in Fig. 2. The experiment was performed at atmospheric pressure using a batch reactor. First, beef tallow and the catalyst were loaded into the reactor. The substrate was heated to the desired temperature. The tallow in the liquid phase was vaporized into the gas phase and ready for cracking. The oil in the gas phase was circulated inside the reactor for catalytic cracking. After the reaction, the gas products leaving the reactor were cooled to 40°C in the condenser unit. The liquid product was collected in a glass liquid sampler at room temperature. Then, the liquid product was distilled at 350°C, where the final light liquid fuel was obtained.

2.5. Experimental Design

A statistical design of experiments eliminates the systematic errors with an estimate of the experiment error and minimizes the number of experiments [25]. The experiments were conducted with three response variables in central composite design. Temperature, reaction time and catalyst loading were independent variables in the experiment, each was considered at five levels, namely –α, -1, 0, +1 and +α (where α is equal to 1.68), shown in Table 3.

The regression equation model was applied to estimate the responses on the basis of a second-order polynomial model shown in Eq. (1). In order to carry out a comprehensive analysis of the catalytic cracking process, three main dependent responses were considered which were: yield liquid fuels, defined as Eq. (2).. The model terms were selected or rejected based on the p values with 95% confidence level. The results were completely analyzed using analysis of variance by Minitab software.

$$Y = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_3 X_3 + \alpha_{12} X_1 X_2 + \alpha_{13} X_1 X_3 + \alpha_{23} X_2 X_3 + \alpha_{11} X_1^2 + \alpha_{22} X_2^2 + \alpha_{33} X_3^2 \quad (1)$$

$$Y = \frac{m_{liquid\ product}}{m_{beef\ tallow}} \quad (2)$$

where Y is the predicted response, α_0 model constant; X_1, X_2 and X_3 are the coded values of the independent variables; α_1, α_2, and α_3 are linear coefficients; α_{12}, α_{13}, α_{23} are cross product coefficients; and α_{11}, α_{22}, α_{33} are the quadratic coefficients.

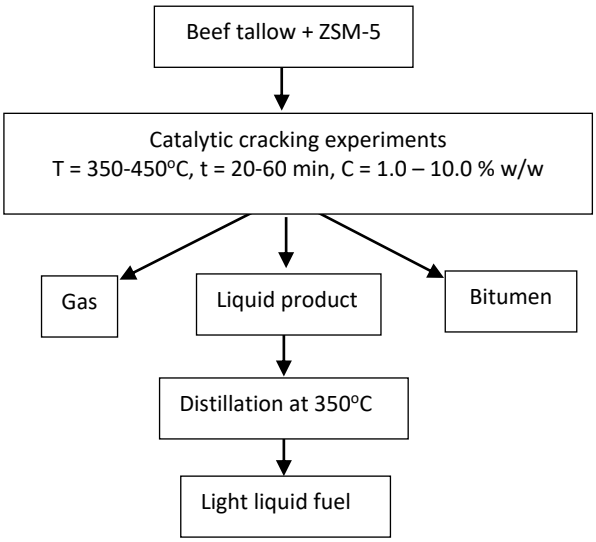


Fig. 2. Catalytic cracking procedure

Table 3. Experimental parameters and levels used for the experimental design.

Parameters	level				
	-α	-1	0	+1	+α
Temperature, X_T (°C)	350	370	400	430	450
Reaction time, X_t (min)	20	32	40	52	60
Catalyst loading, X_C (% w/w)	1.0	2.8	5.5	8.2	10.0

Table 4. Liquid product conversion as a function of temperature, time and catalyst loading.

Test	Temperature (°C)	Time (min)	Catalyst loading (% w/w)	Conversion (%)
1	370	32	2.8	8.7
2	370	32	8.2	9.3
3	370	52	2.8	11.3
4	370	52	8.2	12.7
5	430	32	2.8	52.7
6	430	32	8.2	55.3
7	430	52	2.8	69.3
8	430	52	8.2	70.7
9	400	40	5.5	51.3
10	400	40	5.5	51.0
11	400	40	5.5	51.2
12	400	40	5.5	50.7
13	400	40	5.5	50.7
14	400	40	5.5	51.0
15	350	40	5.5	10.7
16	450	40	5.5	50.7
17	400	20	5.5	49.7
18	400	60	5.5	59.3
19	400	40	1.0	49.3
20	400	40	10.0	52.3

2.6. Product Characterization

Properties of the light liquid fuel (total acid number, heating value, viscosity and density) were measured using similar standard procedures used for petroleum products. The total acid number determined the acidity level by ASTM D664. The heating value of light liquid product was tested using an oxygen bomb calorimeter according to ASTM 4809. The viscosity was measured using a saybolt universal viscometer based on ASTM D88 . Finally, the density was analyzed according to ASTM D4052. Gas chromatographic – mass spectrometric (GC–MS) analysis was conducted using Agilent model 7890A gas chromatograph equipped with Agilent 5975C mass selective detector. The gas chromatograph was fitted with a DB-5 MS capillary column (30 m x 0.25 mm ID, 0.25 µm film thickness). The injector was detemined at 250°C and helium was the carrier gas. The oven was hold at 40°C for 4 min, then heated to 280°C at a rate of 10 °C/min.

3. Results and Discussion

3.1. Conversion of Tallow to Liquid Product

The catalytic cracking of beef tallow produced liquid products, gases, and solid residues. In this work, we focused on conversion of original beef tallow into liquid product. Experimental results of catalytic cracking of tallow are summarized in Table 4, against test conditions designated from the statistical design. The conversion of tallow to liquid product obtained was between 8.6 to 70.7% w/w. It was shown that temperature, reaction time, and catalyst loading affected the conversion. Based on the results, it can be seen that the liquid product converted was quite low at temperatures below 400°C for all condition considered, similar to those reported in the literature [14]. Therefore, the appropriate reaction temperatures should be 400°C or higher. From central composite design of experiments, the best-fitting models were determined by multi-regression and backward elimination from the experimental data. The polynomial model for the conversion was regressed by discussing the significant terms. A good correlation between the experiment and the prediction was evident with R^2 = 0.916. The predicted model for the conversion into liquid product is shown in Eq. (3), where Y = conversion (% w/w); X_T = temperature (°C); X_t = reaction time (min); X_C = catalyst loading (% w/w).

$$\begin{aligned} Y = & -1722 + 8.9X_T - 5.4X_t + 1.9X_C + 0.014X_T X_t \\ & + 0.003X_T X_C - 0.003X_t X_C - 0.011X_T^2 \\ & + 0.002X_t^2 - 0.245X_C^2 \end{aligned} \quad (3)$$

Linear terms (X_T and X_t) were observed to be significant, whereas all quadratic terms did not show strong correlation. The optimum values of operating variables were obtained by solving the regression equation with Minitab software. Then, the optimal condition for liquid product conversion by

catalytic cracking approximated by the model equation was T = 443ºC, t = 60 min and C = 6.3% w/w, and the theoretical liquid conversion predicted was 78.5% w/w. To compare with the prediction by the model, the experiment was carried out at the optimum conditions for at least three times, where average liquid conversion was 74.8% w/w which was closely similar to the prediction value from the model equation. Validity of the empirical model was therefore confirmed by the experimental verification.

Figs. 3 and 4 show the contours of the effect of temperature and catalyst loading at a fixed reaction time of 40 min, and the effect of temperature and reaction time at a fixed catalyst loading of 5.5% w/w on conversion of the liquid product. The temperature and reaction time showed important effect in yielding high amount of liquid product. A tendency was clearly evident that the conversion improved with temperature and time. It was expected that more severe temperature and extended period would improve the liquid conversion, for the reaction. But, excessive heating at prolonged period may lead to serious energy loss and material integrity issue, as well as likeliness of undesirable by-product formation.

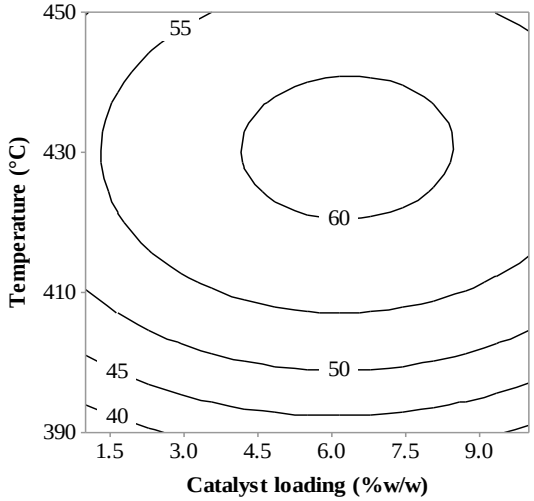


Fig. 3. Contour of the effect of catalyst loading and temperature on conversion of liquid product with a constant reaction time.

3.2. Analysis of Light Liquid Fuel

It has been acknowledged that reaction steps in decomposition of triglyceride with the presence of a catalyst include the thermal breakdown of the triglyceride, followed by deoxygenation, thermal and catalytic cracking into paraffin and olefin hydrocarbons, and subsequent conversions into light olefins, aromatics and aliphatics by catalytic mechanisms [14]. In this work, the light liquid fuel was obtained from the liquid product with additional distillation. GC-MS analysis of the light liquid fuel yielded the main thermal and catalytic cracking products which are displayed in terms of compound and peak time in Fig. 5.

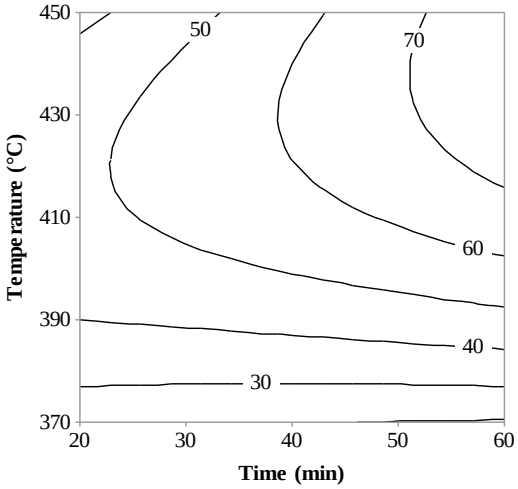


Fig. 4. Contour of the effect of reaction time and temperature on conversion of liquid product with a constant catalyst loading.

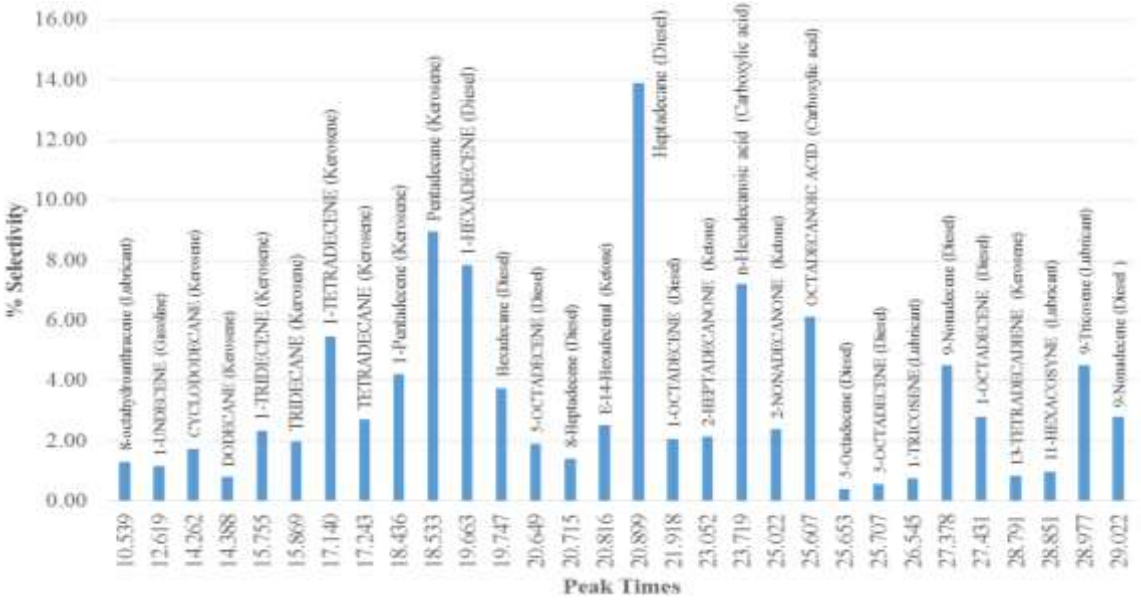


Fig. 5. GC-MS analysis of light liquid fuel.

Table 5. Physical properties of light liquid fuel obtained from this work.

Parameter	Unit	ASTM method	Light liquid fuel	Beef allow	Commercial fuels		
					Gasoline	Kerosene	Diesel
Heating value	MJ/kg	4809	45.8	36.64	44.39-47.29	42.99-46.19	43.79-44.79
Viscosity @40°C	cSt	D88	3.2	46.37	0.5-0.6	1.3	2.8-5.0
Density	kg/m^3	D4052	870	929	719.7	780-810	832
TAN	mg_{KOH}/g	D664	142.27	5.3	n/a	n/a	n/a

They were linear, common long-chain hydrocarbons (decanes, nonenes) and oxygenated organic compounds (carboxylic acids and some ketones). The main chemical compositions of products were hydrocarbons C_6-C_{48}. Based on selectivity defined as ratio between sum of peak areas of interested group and total peak areas, the light liquid fuel was divided into three groups: gasoline containing carbon atoms ranging from C_7 to C_{11}, kerosene containing carbon atoms C_{12} to C_{15}, and diesel containing carbon atoms C_{16} to C_{21} [14]. The light liquid fuel obtained from this work was found to contain high proportions of kerosene (35.8%) and diesel (28.9%), in similar range to those reported in the literature for palm oil and animal fats [2, 15, 18-20].

Table 5 shows the physical properties of the light liquid products, original beef tallow, and commercial fuels. The light liquid products were quite acceptable when compared against values specified for commercial fuels. The heating value was 45.8 MJ/kg which was higher than the beef tallow and in similar range to gasoline and kerosene. The viscosity of light liquid product was 3.2 cSt which was smaller than the tallow and in the similar range to diesel. With repeat to density, it was found to be similar to diesel. Finally, the total acid number was relatively high because the beef tallow was broken down into liquid fuels containing hydrocarbons and carboxylic acids or fatty acids with smaller molecules. When the number of acid molecules in light liquid product were analyzed, they were more abundant, compared to beef tallow which contained mostly triglycerides and fatty acids.

4. Conclusion

Production of diesel-like biofuels from waste animal fats by catalytic cracking is a promising energy option. In this work, catalytic pyrolysis of beef tallow into liquid product with ZSM-5, and subsequent distillation into light liquid fuel were studied. Conversion of beef tallow into the liquid product was dependent on process variables. Temperature, reaction time, and catalyst loading were found to affect the liquid product from catalytic cracking of beef tallow. From the design of experiments adopted, the prediction model for the conversion of beef tallow into liquid product was derived. The optimum condition for cracking tallow was found at temperature of 443°C, reaction time of 60 min, catalyst loading at 6.3% w/w. Chemical analysis of the light liquid fuel showed kerosene (35.8%), and diesel (28.9%) to be major fractions. The physical properties of the light liquid fuel were found to be similar to diesel. This study shows that there is a potential for producing diesel-like hydrocarbon fuel from catalytic cracking of beef tallow, however, evaluation of cost effectiveness of the process should be addressed.

Acknowledgements

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