CONVERSION OF WASTE CHICKEN FAT TO LIQUID FUEL ON COAL FLY ASH CATALYST BY CATALYTIC CRACKING

Miss Phorndranrat Suchamalawong

การเปลี่ยนของเสียไขไก่เป็นเชื้อเพลิงเหลวบนเถ้าลอยถ่านหินโดยการแตกตัวเชิงเร่งปฏิกิริยา

น.ส.ภรณ์ดรัลรัตน์ สุชามาลาวงษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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CHULALONGKORN UNIVERSITY

ภรณ์ครัลรัตน์ สุชามาลาวงษ์ : การเปลี่ยนของเสียไขไก่เป็นเชื้อเพลิงเหลวบนเถ้าลอยถ่านหินโดยการแตกตัวเชิงเร่ง
ปฏิกิริยา. (
CONVERSION OF WASTE CHICKEN FAT TO LIQUID FUEL ON CO
AL FLY ASH CATALYST BY CATALYTIC CRACKING) อ.ที่ปรึกษาหลัก :
ศ. ดร.ธราพงษ์ วิทิตศานต์

งานวิจัยนี้ศึกษาภาวะที่เหมาะสมของการการแตกตัวเชิงเร่งของของเสียไขไก่ไปร่วมกับการใช้ตัวเร่งปฏิกิริยาเถ้าลอย
ถ่านหินเพื่อผลิตเชื้อเพลิงเหลวและออกแบบการทดลองเชิงตัวประกอบแบบสองระดับ (2^k factorial design) เพื่อศึกษา
อิทธิพลของตัวแปรที่มีผลต่อร้อยละผลได้ของผลิตภัณฑ์ของของเหลว แนฟทาและดีเซล การทดลองแบ่งออกเป็น 2 ส่วน ส่วน
แรกเป็นการดำเนินการทดลองด้วยเครื่องปฏิกรณ์ขนาดเล็กแบบแบตช์ขนาด 70 มิลลิลิตร โดยศึกษาอิทธิพลของตัวแปรที่ส่งผล
ต่อการแตกตัวเชิงตัวเร่ง ที่อุณหภูมิ 420 - 460 องศาเซลเซียส ระยะเวลาของปฏิกิริยา 45 - 75 นาที ความดันแก๊ส
ไฮโครเจนเริ่มต้น 1 - 5 บาร์ และเถ้าลอยของถ่านหินร้อยละ 1 ถึง 5 โดยน้ำหนัก วิเคราะห์องค์ประกอบของผลิตภัณฑ์
เชื้อเพลิงเหลวด้วยเครื่องแก๊สโครมาโทกราฟจำลองการกลั่นตามคาบจุดเดือด ตามมาตรฐาน ASTM D2887 ใช้โปรแกรม
design-expert หาภาวะที่เหมาะสม พบว่าภาวะดำเนินการที่อุณหภูมิ 445 องศาเซลเซียส ระยะเวลาในการทำปฏิกิริยา
45 นาที ความดันไฮโครเจนเริ่มต้น 1 บาร์ ให้ปริมาณร้อยละผลได้ของผลิตภัณฑ์เชื้อเพลิงเหลวสูงสุดคือ 76.62 โดยน้ำหนัก
องค์ประกอบของเชื้อเพลิงเหลวประกอบด้วยร้อยละผลได้แนฟทา 21.33 และร้อยละผลได้ดีเซล 31.00 โดยน้ำหนัก
เชื้อเพลิงเหลวที่ได้มีค่าความร้อน 42.96 เมกะจูลต่อกิโลกรัม และค่าความเป็นกรด 13.51 มิลลิกรัมโพแทสเซียมไฮดรอก
ไซด์ต่อกรัมน้ำมัน อัตราการเปลี่ยนของกากน้ำมันเป็นผลิตภัณฑ์ ณ ช่วงเวลาต่างๆ ถูกนำมาศึกษาจลนพลศาสตร์ พบว่าการแตก
ตัวเชิงเร่งของของเสียไขไก่ไปเป็นเชื้อเพลิงเหลวร่วมกับการใช้เถ้าลอยถ่านหินมีอัตราการเกิดปฏิกิริยาเป็นอันดับ 2 โดยพลังงาน
กระตุ้นของปฏิกิริยามีค่าเท่ากับ 85.97 klmol^{-1} และ แฟกเตอร์ความถี่คือ 1.01×10^3 ต่อวินาที ส่วนที่สองศึกษาภาวะ
เหมาะสมในการผลิตเชื้อเพลิงเหลวในเครื่องปฏิกรณ์ต่อเนื่องขนาด 3 ลิตร ตัวแปรที่ศึกษาประกอบด้วยอุณหภูมิในการทำ
ปฏิกิริยา 420-460 องศาเซลเซียส อัตราการป้อนน้ำมัน 3-9 มิลลิลิตรต่อนาที อัตราการไหลของแก๊สไนโตรเจน 50-150
มิลลิลิตรต่อนาที และปริมาณตัวเร่งปฏิกิริยาร้อยละ 30-60 โดยปริมาตรของเครื่องปฏิกรณ์ จากการใช้โปรแกรม design-
expert หาภาวะที่เหมาะสม พบว่าภาวะดำเนินการที่อุณหภูมิ 460 องศาเซลเซียส อัตราการป้อนน้ำมัน 9 มิลลิลิตรต่อนาที
อัตราการไหลของแก๊สไนโตรเจน 50 มิลลิลิตรต่อนาที และปริมาณตัวเร่งปฏิกิริยาร้อยละ 60 โดยปริมาตรของเครื่องปฏิกรณ์
ให้ปริมาณร้อยละผลได้ของผลิตภัณฑ์เชื้อเพลิงเหลวสูงสุดคือ 76.76 โดยน้ำหนัก องค์ประกอบของเชื้อเพลิงเหลว
ประกอบด้วยแนฟทาร้อยละ 21.62 และดีเซลร้อยละ 41.65 โดยน้ำหนัก ศึกษาประสิทธิภาพของตัวเร่งปฏิกิริยาพบว่า
ตัวเร่งปฏิกิริยาเถ้าลอยถ่านหินใช้งานได้เป็นเวลา 7 ชั่วโมง จากนั้นประสิทธิภาพจะเริ่มลดลงเนื่องจากแคลเซียมออกไซด์
เปลี่ยนเป็นแคลเซียมไฮดรอกไซด์ ผลวิเคราะห์สมบัติทางเชื้อเพลิงให้ค่าความร้อน 43.39 เมกะจูลต่อกิโลกรัม และค่าความ
เป็นกรด 3.82 มิลลิกรัมโพแทสเซียมไฮดรอกไซด์ต่อกรัมน้ำมัน

สาขาวิชา   วิทยาศาสตร์สิ่งแวดล้อม   ลายมือชื่อนิสิต ....

ปีการศึกษา   2561   ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

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CONVERSION OF WASTE CHICKEN FAT TO LIQUID FUEL ON COAL FLY ASH CATALYST BY CATALYTIC CRACKING. Advisor: Prof. Tharapong Vitidsant, Ph.D.

In this research work, a study on the catalytic cracking of waste chicken fat

(WCF) on fly ash to liquid fuels and using 2k factorial design to determine the influence of parameters on liquid yield, naphtha and diesel content was investigated. The research was divided into 2 parts. First, the experiment was carried out in a batch lab scale reactor of 70 mL. The objectives are to determine the influence of parameters that affected the %yield of liquid product naphtha and diesel–liked fuels at the operating conditions of temperature range of 420 - 460 ˚C, reaction time 45-75 minutes, initial hydrogen pressure of 1-5 bar and coal fly ash loading of 1-5 %wt. The liquid product was collected and analyzed using simulated distillation gas chromatography according to ASTM2887. Data of experiments were analyzed by design-expert program, the results showed that the optimal condition was operated at a temperature of 445 ˚C, the reaction time of 45 minutes, the initial pressure of hydrogen 1 bar, coal fly ash loading of 1%wt, which obtained the highest liquid yield of 76.76 %wt., whereas the liquid product consisted of 21.50 %wt. naphtha and 31.00 %wt. diesel. The liquid product has the heating value of 42.92 MJkg^{-1} and the acid value is 13.51 mgKOHg^{-1}. The kinetics study was examined due to the conversion change of long residue with the reaction time. The results indicated the second order with respect to long residue, the activation energy (Ea) 85.97 kJmol^{-1} and frequency factor (k0) 1.01×103 s^{-1}. The experiment in the second part was focused on the production of liquid fuel in 3 L continuous reactor. The ranges of study variables were as follows: temperature of 420-460 ˚C, flow rate of waste chicken fat of 3-9 mL/min, N$_2$ gas flow rate of 50-150 mL/min and amount of catalyst 30-60 % (occupied by reactor volume). From design-expert program, it was found that the optimal condition of continuous reactor were temperature 460 ˚C, flow rate of waste chicken fat 9 mL/min, N2 gas flow rate 50 mL/min and amount of catalyst 60 % of reactor volume, gave the highest yield of liquid, naphtha and diesel were 76.76, 21.62 and 41.65 %wt, respectively. The coal fly ash catalyst was determined the catalyst efficiency, it was found that fly ash activity is stable during 7 hours and after

Field of Study:	Environmental Science	Student's Signature ....
Academic Year:	2018	Advisor's Signature ....

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CHAPTER 1
INTRODUCTION

Nowadays, there is a high demand of energy because the rapid growth of the economy, society, and industrial, therefore, soon, the lack of an energy crisis is foreseeable if the new sources of energy have not been found. In addition, fossil fuel burning has enormous impact on the environment, particularly on climate change, which is one of the main focusing issues. That is the reason why it is necessary to develop and enhance technologies. Over the past decades, many researchers put effort into investigation of new kinds of energy sources that can be replaced fossil fuel such as natural energy, solar energy, hydroelectric energy, biomass energy, and energy from waste.

In the present, waste to energy principle is wildly popular as many countries have been utilized it. The essential part is the processing technology that allows the conversion of these resources into renewable energy. To demonstrate, the generation of electricity from solid wastes, production of solid fuel from municipal waste, production of biogas from wastes, or producing fuel from waste. [1-4]

Thailand is one of the important players in the food industry. The food industry plays a crucial economic role and has a strong influence on the country's income and export value. The export value of food processing is expected to continually increase. To illustrate, according to GAIN Report Number: TH7116 date 9/1/2017 on the topic of "Thailand Poultry and Products Annual 2017", in 2018, Thailand domestic consumption rate is expected to sharply grow at 4 - 5 percent as compared to 3 percent growth in 2017, moreover, especially, in chicken meat exports, which enormously grow by 12 percent to 770,000 MT in 2017 and will be an on-going-growth of 4 percent in 2018 [5].

On the fact that the growth of chicken meat exports sharply augmented, fat waste is in the light of attention on waste water management because the fat waste is an organic compound that has a significant impact on the quality of water. The high level of fat waste is especially found in water released from the meat processing

facilities. The drain water, which contains high levels of fat wastes, provides an environment that is rich in organic compounds that promotes oxidation and growth of micro-organisms. This has a negative effect on the dissolved oxygen content. Animals, plants, and the ecosystem to suffer from fat contamination and low oxygen levels when this drain water is released into public water sources. At critical amounts of fats, the water surface is covered by the fat leading to anaerobic digestion. As a result, methane and hydrogen sulfide is released and fills in the air with their characteristic odor and polluting water with black or dark color [6].

In the meat industries, fat waste separate from water and collected in the fat trap tank for sanitary disposal in the landfill. Although dumping the fat is an easy method of treatment, the soil may be contaminated. The cost and pollution from landfill will decrease if such fat can be utilized as a renewable energy source. Chicken fat wastes are formed mainly of triglycerides that can be converted to an organic liquid product (OLP). OLP is a cheap and abundant resource that can be used in generating alternative energy. With suitable waste management, food processing facilities can potentially provide a reliable source of OLP.

Several processes have been proposed to produce biofuel from biomass waste, but thermo-chemical process is the most popular process for converting waste hydrocarbon compounds to biofuel. Pyrolysis and catalytic cracking are two commonly utilized thermochemical conversion techniques. Each of the process generates solid, liquid and gas products. The liquid product from pyrolysis and catalytic cracking consists of a complex hydrocarbon compounds, that also different functional groups and molecular sizes which can be used as fuel after a catalytic upgrading process [7-10]. Catalytic cracking uses a lower process conditions than a pyrolysis process where long chain hydrocarbon is cracked into small chain hydrocarbon by a combination of decarboxylation, deoxygenation, dehydration and dehydrogenation reactions to form a diesel-like fuels, which can be used as a petroleum fuel replacement. The esterification process has a weak point, it uses a large of quantity of methyl or ethyl ester while producing a glycerol as a by-product. Consequently, esterification method is well

known, but a limited process while catalytic cracking has potential to be developed further with advances in catalyst engineering.

Coal fly ash is the wastes from a thermal power plant. The disposal of coal fly ash has become an environment problem. It needs an abundant vacant area for dumping and/or landfill, the ash makes a cost of ash dams. Fly ash is a complex mixture composed of high quantities of SiO_2, Al_2O_3, MgO, CaO, and Fe_2O_3. Z.T. Yao et al. [11], studied the application of fly ash as a catalyst in chemical processes, the result indicated that fly ash mostly includes of various metal oxide and advance content of iron oxides shown heat resistance from the high temperature. Missengue et al. [12], investigated the use of fly ash, as a low-cost source SiO_2, Al_2O_3 in zeolite synthesis. The effective utilisation of coal fly ash as a catalyst for thermal cracking processes would not only remedy environmental problems, but also help in value-added with the economically natural resources.[13, 14]

The main purpose of this research is the utilisation of fly ash, typically considered as waste, as a low-cost catalyst in the catalytic cracking process. Waste chicken fat can be used as feedstock for biofuel production. The aims of the current research determine an optimum condition to produce biofuel and investigate the several process conditions which affected to the temperature, reaction time, catalyst loading and H_2 pressure on the catalytic cracking process that uses fly ash. The 2^k factorial design was performed to investigate the variables and optimisation. The liquid products were characterised for fuel properties according to the standard test and comparison between conventional petroleum fuel products. Furthermore, kinetic parameters such as Activation Energy, reaction order and pre-exponential factor were obtained.

Objectives

       1. To investigate variables that affect the catalytic cracking of waste chicken fat on the product distribution.

       2. To determine the optimum condition with the highest percentage of liquid fuel product yield.

       3. To study the kinetics of catalytic cracking to predict pathway of the cracking process.

Research hypothesis

       1. Catalytic cracking of waste chicken fat is a breakdown of fatty acids into small hydrocarbon chains with coal fly ash as the catalyst. The catalyst properties are like the acid heterogeneous catalysts type. It should be possible to promote accelerated decomposition and liquid fuel quality upgrading close to commercial fuel property (naphtha and diesel).

       2. Determination of an optimum condition by two- level factorial experimental design and finding the variable's influence on the conversion of waste chicken fat into liquid fuel. Using the Design Expert Version 11.0.0 (Stat Ease, USA) program, it is possible to predict the optimum conditions for conversion of waste chicken fat into fuel that produces the highest quantity and quality of liquid product.

       3. Thermal decomposition and catalytic cracking are complex reactions. Kinetics study can predict the progress of the decomposition reaction, as well as the direction of reaction.

Scope of study

       Determine the variables that influence the conversion of waste chicken to liquid fuel with coal ash catalytic cracking. In this research, two-level factorial design of experiment was used to investigate the percentage yields of fluid and product selectivity of a similar commercial fuel. To study suitable conditions for using coal fly ash as catalyst in batch and continuous reactors to produce the highest proportion of oil and the qualities of oil relate to hydrocarbon fuel products. Additionally, investigating the pathway of the decomposition reaction by studying kinetics in a batch reactor, determine the order of reaction, activation energy and pre-exponential factor.

Conceptual Framework
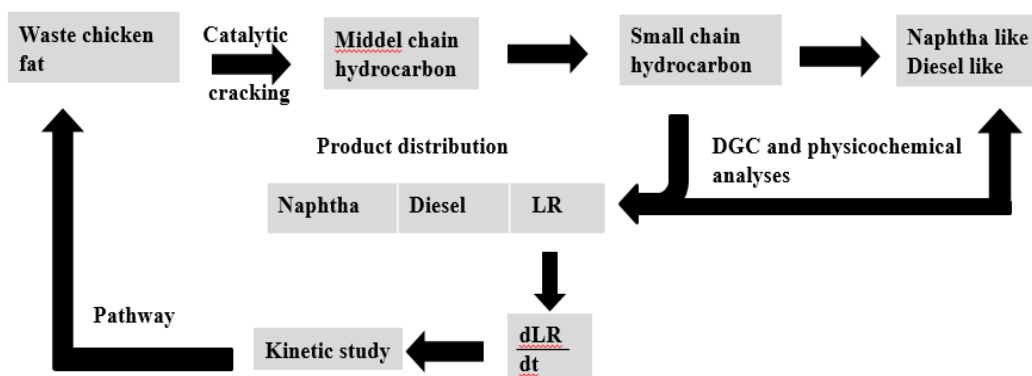
Research methodology

1. The method of the reactor, theory and literature reviews were investigated.

2. Calcination of coal fly ash catalyst with temperature of 600 ˚C, for 1 hour.

3. Characterizing the primary properties of waste chicken grease including physical properties, thermo gravimetric analysis (TGA) technique, chemical composition, fatty acid composition, the boiling point range, and the ultimate analysis.

4. Characterizing properties of fly ash catalyst including compositions by XRF, determine the surface area by BET and study formation by SEM.

5. Design of experimental using two-level factorial design. The table was shown the variable parameters in this research.

Variable parameters	
Batch reactor	Continuous reactor
Effect of temperature on catalytic cracking at 420-460°C	Effect of temperature on catalytic cracking at 460-420°C
Effect of reaction time on catalytic cracking at 45-75 min	Effect of feeding rate on catalytic cracking at 3-9 ml/min
Effect of catalyst content on catalytic cracking at 1–5 %wt.	Effect of N_2 gas flow rate on catalytic cracking at 50- 150ml/min
Effect of initial hydrogen gas pressure on catalytic cracking at 1-5 Bar	Effect of catalyst content on catalytic cracking at 30-60%wt.

6. Using 2^k factorial experimental design to find the parameters which are affected to

The catalytic cracking reaction of waste chicken fat and Design expert program for the

optimum condition finding.

7. Characterizing liquid product.

   7.1 To determine the product distribution of liquid fuels by simulated Distillation

      Gas Chromatograph (DGC)

   7.2 To determine the heating value of liquid product

   7.3 To determine the acidity properties in liquid product.

   7.4 To determine the ultimate analysis of liquid product.

   7.5 To determine the composition of liquid product by GC-MS

8. Kinetic study was carried out on the process condition of

   • Temperature of 410- 470˚C.

   • Reaction time of 0-75 minutes

   Whereas the initial hydrogen pressure and content of fly ash also kept constant at 1

   bar and 1%wt respectively. Reaction order of catalytic cracking of waste chicken fat

   in batch reactor, as well as activation energy (E_a) and the pre-exponential factor (k_0)

   from Arrhenius equation.

9. Data analysis, conclusion, write a thesis and research publications.

Expected Benefits

1. To know the optimum condition of catalytic cracking of waste chicken fat using coal fly ash catalyst. To perceive the reaction order in order to predict the waste chicken fat with catalytic cracking mechanism.

2. To obtain the high-quality liquid produced fuel that is close to petroleum fuel.

3. To scale-up the process condition for the commercial production of waste chicken fat conversion to liquid.

CHAPTER 2
THEORY AND REVIEWS

2.1 Animal Fat

Animal fats are obtained by meat animal processing facilities and rendering process. Animal fats consist essentially of fatty acid esters and glycerin mixtures, and are known as triglycerides[15]. A triglyceride consists of a three carbon glycerol head group to which are added three fatty acid chains [16]. A structure of triglycerides is shown in Fig. 2.1. All triglycerides have the same basic structure, and the differences in properties and use of commercial triglycerides depend largely on the length, degree of unsaturation and other chemical modifications to the fatty acid chains [17, 18].

Fatty acids are allocated into two groups:

2.1.1 **Saturated fatty acids** are fatty acids in which the bonds between carbon atoms in a molecule are single bonds and cannot accept additional hydrogen. The general chemical formula is $C_nH_{2n+1}COOH$. It is stable, does not react with oxygen (so there is no lipid oxidation), and has a high melting point compared to unsaturated fatty acids with equal carbon atoms. The most common saturated fatty acid is palmitic acid (C16:0) found in animal fat, coconut oil and palm oil, etc.

2.1.2 **Unsaturated fatty acids** are fatty acids in which the bonds between the carbon atoms in a molecule are double bonds at one or more positions. Unsaturated fatty acids are commonly found in many vegetable oils such as rapeseed oil, corn oil and olive oil. The most abundant unsaturated fatty acid in vegetable oil is oleic acid (C18:1) and linoleic acid (C18:2)

Examples of the structures of common C18 fatty acids are given in Fig. 2.2, as C18:0 (stearic acid, octadecanoic acid), C18:1 (oleic acid, 9-octadecenoic acid) and C18:2 (linoleic acid, 9,12-octadecenoic acid) (8). Typical fatty acid composition of tallow and other animal fats is given in Table 2.1. These triglycerides have higher viscosity and therefore cannot be used as fuel in common diesel engines (ibid) but will need to be refined to conform to diesel properties. Technologies such as biochemical, thermo-chemical, physical and chemical processes are available for recovering bio-fuels from triglyceride-based materials. Thermochemical processes include

gasification, pyrolysis and combustion. Among these technologies, pyrolysis is favored because it is simple and inexpensive to construct [19].
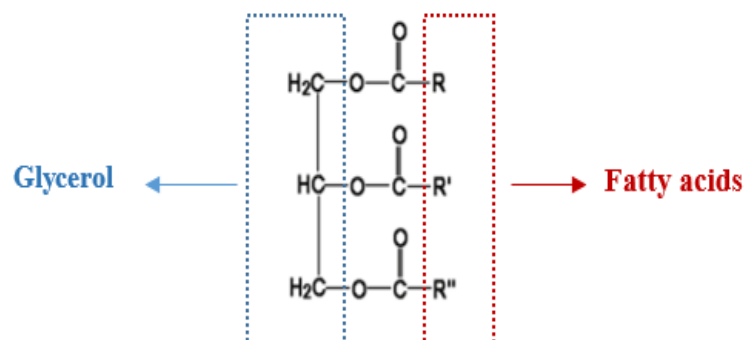
Fig. 2.1 Molecular structure of triglyceride.
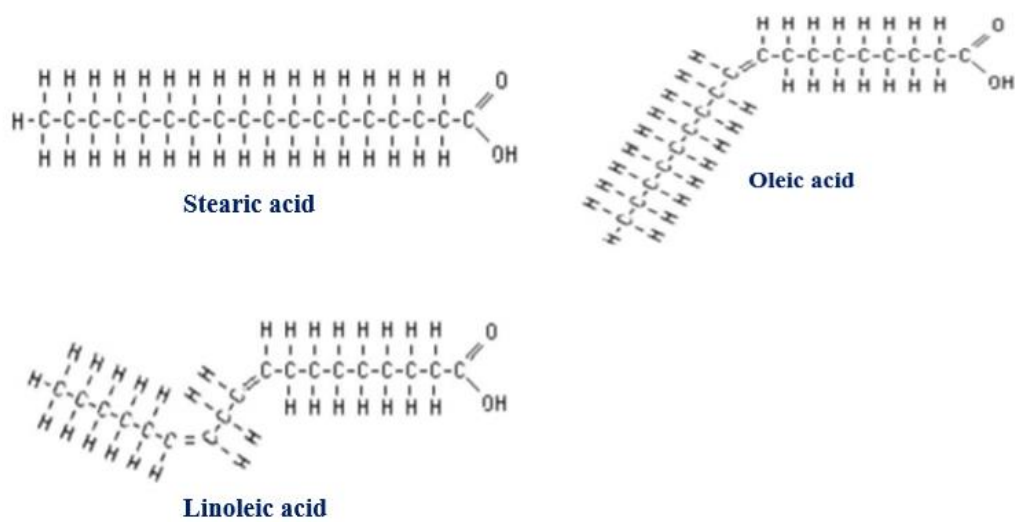
Fig. 2.2 Structure of common fatty acids.

Table 2.1 Typical fatty acid composition (%wt.) of major animal fats. Fatty acid includes the length of carbon chain and amount of double bonds [19].

Fatty acid	Fat (%wt.)				
	Chicken fat	Beef tallow	Lard	Mutton tallow	Butter
Myristic (C14:0)	1.00	3.00	2.00	6.00	12.00
Palmitic (C16:0)	22.00	27.00	26.00	27.00	26.00
Palmitoleic (C16:1)	6.00	11.00	5.00	2.00	3.00
Stearic (C18:0)	7.00	7.00	11.00	32.00	11.00
Oleic (C18:1)	40.00	48.00	44.00	31.00	28.00
Linoleic (C18:2)	20.00	2.00	11.00	2.00	2.00
Other	4.00	2.00	1.00	0.00	18.00

2.2 Biofuel production techniques

Most techniques exist to reduce the potentially high viscosity of biofuels made from animal fats and eliminate any operational problems from its use in a common diesel engine: direct use and blending, thermal cracking (pyrolysis) and trans-esterification (alcoholysis).

2.2.1 Direct use and blending

The main issues of direct use of animal fats as fuel in diesel engines are their high viscosity and poor volatility. Some investigators have attempted to directly inject animal fats into an unmodified diesel engine. Senthil Kumar et al.[20] preheated animal fat at different temperatures before injection in to a single- cylinder direct injection diesel engine with a rated power of 2.8 kW at 1500 rpm. The preheated animal fat showed a reduced ignition delay, reduced combustion duration, arise in peak pressure and lower smoke emissions than diesel.

2.2.2 Pyrolysis

Pyrolysis or cracking involves the thermal decomposition of organic material to smaller molecules through the application of heat without the addition of air or oxygen.

Thermal cracking of triglyceride materials (animal fats) represents an alternative method of producing renewable bio-based products suitable for use in fuel and chemical applications. Adebanjo et al.[21] investigated the production of diesel-like fuel and other value-added chemicals from the pyrolysis of lard and reported the potential for producing diesel-like liquid and a high calorific-value gaseous fuel through lard pyrolysis.

2.2.3 Trans esterification reaction

Trans-esterification is the most commonly used method to reduce viscosity of animal fats. It generates products commonly known as biodiesel. However, the disadvantage of this conventional trans-esterification process is its efficiency, which depends on the quality of fats and oils. Therefore, it is the need of hour to develop a more benign and integrated process, which can utilize low quality fats and oils containing higher level of free fatty acids (FFA), to produce biodiesel in cost-effective manner. A problem of using high FFA containing fats and oils to produce biodiesel is the formation of soaps due to emulsion formation [22-25].

2.3 Cracking process

The animal fat waste is suitable as biofuel feedstock to cracking process because it is composed of fatty acids such as 10-octadecenoic acid and hexadecanoic acid. This carbon chains can be cracked into hydrocarbons with shorter carbon chains that have conformity with the nature of fossil fuels.

2.3.1 Thermal cracking [26, 27]

Thermal decomposition of triglycerides produces compounds of classes including alkane, alkenes, alkadienes, aromatics and carboxylic acids. Thermal decomposition of its structures proceeds through either free-radical or carbonium ion mechanism as shown below

1. Decompostion of triglyceride

$$\begin{array}{c} CH_2OCOR' \\ | \\ CHOCOCH_2R'' \\ | \\ CH_2OCOR'' \end{array} \longrightarrow \begin{array}{c} CH_2 \\ | \\ CH \\ | \\ CHO \end{array} + R'COOH + R'''COOH + R''CH=CO$$

(2.1)

2. Decomposition of free fatty acids

$$RCOOH \longrightarrow CO_2 + RH \tag{2.2}$$

$$2\,RCOOH \longrightarrow CO_2 + H_2O + RCOR \tag{2.3}$$
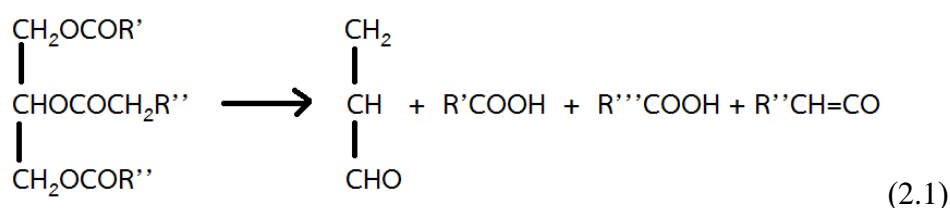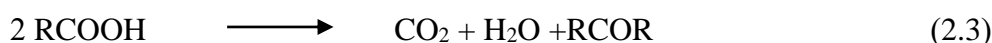
3. Decomposition of ketene and acrolein

$$2R''CH=CO \longrightarrow 2CO + RHC=CHR \tag{2.4}$$

$$CH_2=CHCHO \longrightarrow CO + C_2H_4 \tag{2.5}$$

$$RCOCH_2R \longrightarrow R\text{-}R + CH_2CO \tag{2.6}$$

$$2RCOCH_2R \longrightarrow 2R_2 + CO + C_2H_4 \tag{2.7}$$
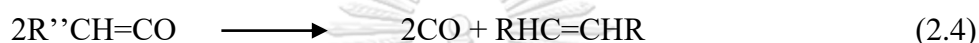
4. Decomposition into elements

$$C_nH_{2n+2} \longrightarrow nC + (n+1)H_2 \tag{2.8}$$
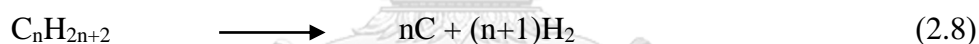
5. Dehydrogenation of paraffins

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2 \tag{2.9}$$

6. Splitting Decomposition of paraffins

$$C_nH_{2n+2} \longrightarrow C_{n-m}H_{2n-2m+2} + C_mH_{2m} \tag{2.10}$$
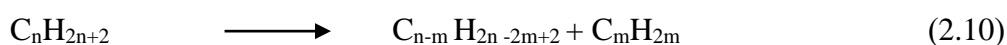
7. Alkylation of paraffins, reverse of number 6

8. Isomerization of paraffins

$$N\text{-}C_nH_{2n+2} \longrightarrow \text{iso-}C_nH_{2n+2} \tag{2.11}$$
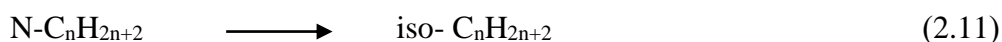
9. Aromatic cyclization of paraffins

$$C_{(2n+6)}H_{(2n+14)} \longrightarrow C_nH_{2n+1} + 4H_2 \tag{2.12}$$

10. Polymerization of paraffins

$$2C_nH_{2n} \longrightarrow C_{2n}H_{4n} \tag{2.13}$$

$$C_nH_{2n} + C_mH_{2m} \longrightarrow C_{(n+m)}H_{2(n+m)} \tag{2.14}$$
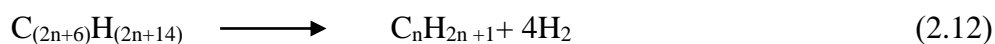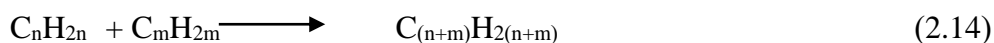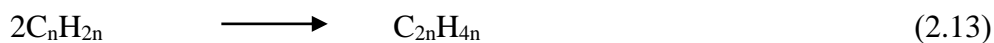
11. Depolymerization of olefins, reverse of number 10

12. Decomposition of olefins to diolefins

13. Decomposition of olefins to acetylenic hydrocarbons

14. Aromatization of cyclization of olefins

15. Hydrogenation of olefins

$$C_nH_{2n} + H_2 \longrightarrow C_nH_{2n+2} \tag{2.15}$$

16. Isomerization of olefins

$$N\text{-}C_nH_{2n} \longrightarrow iso\text{-}C_nH_{2n} \tag{2.16}$$
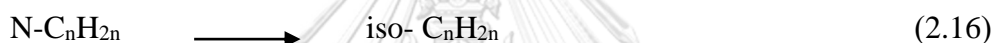
2.3.2. The hydrogen cracking [28, 29]

Cracking along with hydrogen is combination of catalytic cracking and hydrogen addition. The products are high branched molecules including paraffins and naphthene. This reaction starts with carbonium ion formation at acidic surface of catalyst as in equation (2.17).

$$R_1\text{-}CH_2\text{-}CH_2\text{-}R_2 \xrightarrow{\text{Catalyst}} R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 + H^+ \tag{2.17}$$

Carbonium ion may rearrange and eliminate proton from olefins of crack at β-position to give olefins and new carbonium ion as products. After that hydrogenation and dehydrogenation. Olefins in hydrogenation become paraffin compound as in equation 2.18 until 2.20.

$$R_1\text{-}CH_2\text{-}{}^+CH\text{-}R_2 \xrightarrow[-H^+]{\text{B-Scission}} R_1\text{-}CH{=}CH\text{-}R_2 \tag{2.18}$$

$$R_1\text{-}CH_2\text{-}{}^+CH_2\text{-}R_2 \longrightarrow R_2\text{-}CH{=}CH_2 + R_1^+ \tag{2.19}$$

$$R_2\text{-}CH{=}CH_2 + H_2 \xrightarrow{\text{Catalyst}} R_2\text{-}CH_2\text{-}CH_3 \tag{2.20}$$
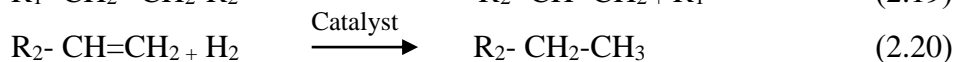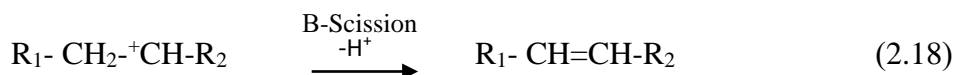
Hydrogenation result in saturated product and hydrogenation at acid site of catalyst also eliminate coke on catalyst surface. Cracking along with hydrogenation is exothermic reaction resulting in high temperature in reactor. It needs to properly control temperature because if the temperature is too high, coke will form and catalyst loss it activity or causes damage to reactor as well as desire product is not formed.

2.4 The catalytic cracking [30-33]

Catalytic cracking has more advantages than other triglyceride processing methods. It can produce various products such as gas, organic liquid product (OLP) and coke. However, large molecules existing in fat cannot easily penetrate deep into smaller 1-2 nm pores of the catalyst and therefore cracking effect is limited to the relatively small reaction sites at the catalyst surface. OLP comprise oxygen compounds (aldehydes, ketones, and carboxylic acids) and hydrocarbons (normal paraffin, naphthenic, and olefin) that match the boiling point ranges of gasoline, kerosene, and diesel. The reaction temperature is lower than that of pyrolysis, and large molecules are broken down into smaller compounds by hydrolysis, dehydrogenation, deoxygenation, and decarboxylation. Compared with transesterification, which converts triglycerides to biodiesel (methyl or ethyl esters of fatty acids), cracking has several advantages such as its low processing cost, and energy consumption for separation process. Additional environmental benefits include the absence of harmful catalysts and wastewater treatment. Catalytic cracking can produce more varied types of fuel such as gasoline and kerosene, among other products as well as diesel fuel.

Important cracking reaction of triglyceride:

1. Hydrolysis of triglyceride: the products are glycerol and free fatty acid as in equation (2.21).

$$CH_2OCOR'$$ $$CH_2$$
$$|$$ $$|$$
$$CHOCOCH_2R'' \longrightarrow CH + R'COOH + R'''COOH + R''CH=CO$$
$$|$$ $$|$$
$$CH_2OCOR'' \qquad CHO$$

(2.21)
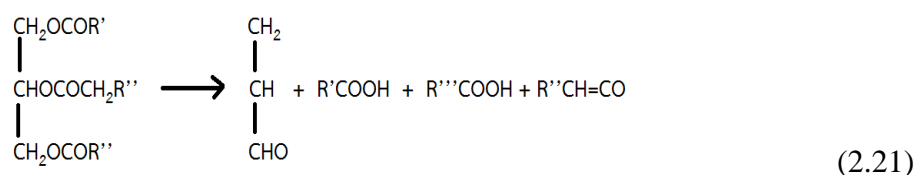
2. Decomposition of free fatty acid: the products are carbon dioxide gas and hydrocarbon compound as in equation (2.22).

$$RCOOH \quad \rightarrow \quad CO_2 + R\text{-}H \qquad\qquad (2.22)$$

3. Decarboxylation: removing of –COOH group (decarboxylation) from fatty acid. The products are hydrocarbon compound and carbon dioxide gas as in equation (2.23).

$$R\text{-}COOH \rightarrow R\text{-}H + CO2 \qquad\qquad (2.23)$$

4. Decarbonylation of ketone give hydrocarbon compound and carbon monoxide as products as in equation (2.24).

$$R\text{-}CHO \rightarrow R\text{-}H + CO \qquad\qquad (2.24)$$

Hydrocarbon compound from reaction according to (2.22), (2.23) and (2.24) is paraffin and olefin which can further react as follow:

6. Cracking of large hydrocarbon molecule into smaller hydrocarbon molecule as in equation (2.25).

$$CH_3\text{-}(CH_2)_4\text{-}CH_2\text{-}CH_2\text{-}\overset{\bullet}{C}H_2 \rightarrow CH_3\text{-}(CH_2)_4\text{-}\overset{\bullet}{C}H_2 + CH_2=CH\text{-}CH_3 \qquad (2.25)$$

7. Large hydrocarbon molecule transfer hydrogen to free radicals as a small hydrocarbon molecule and large hydrocarbon molecule becomes a new free radical which can further react as in equation (2.26).

$$CH_3\text{-}CH_2\text{-}\overset{\bullet}{C}H_2 + CH_3\text{-}(CH_2)_4\text{-}CH_3 \rightarrow CH_3\text{-}CH_2\text{-}CH_3 + CH_3\text{-}(CH_2)_4\text{-}\overset{\bullet}{C}H_2 \qquad (2.26)$$

8. Isomerization transforms the structure of hydrocarbon molecule from straight chain into branch chain structure as in equation (2.27).

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \quad \rightarrow \quad \underset{\underset{CH_3}{|}}{CH_3\text{-}CH\text{-}CH_3} \qquad\qquad (2.27)$$
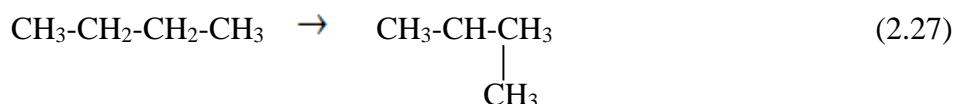
2.5 Catalyst [34-37]

The catalyst is a substance that increase reaction rate or resulting in faster reaction when added to reaction mixture and selective to desired products in any chemical reaction. Catalyst may be or may be not involved in reaction. However, when

the reaction is terminated the catalyst must not be used in the reaction or have to be at the same amount. That is, catalyst is a substance that increases reaction rate without causing any changes to thermodynamic of system. Moreover, adding catalyst make system reach equilibrium faster because it lowers activation energy of the reaction resulting in more molecules with higher energy or equal to activation energy so chemical reaction is faster.

2.5.1 Heterogeneous catalyst

A catalyst in different phase with substrate mostly in solid which used to accelerate reaction of gaseous or liquid substrate. Chemical reaction takes place at the surface of catalyst with sorption-desorption of substrate on catalyst surface as a part of reaction. The advantages of heterogeneous catalysis are such as less toxic of heterogeneous catalyst, can be used in high temperature or high-pressure reaction, easy to separate catalyst from remaining substrate and product, can be reused and longer lifetime.

2.5.2 Heterogeneous reaction mechanism

Reaction pathway of catalyst by heterogeneous catalyst occur on the surface of catalyst always have more than one process with sorption-desorption of substrate on catalyst surface as a part of reaction.

Most of heterogeneous reactions use three phases reactor including of solid as substrate, catalyst, liquid and gas products. Figures 2.3 illustrate the catalysis is realized as a cyclic process with the following steps:

1. Mass transfer: external diffusion is the diffusion of reactants A from fluid stream through the outer surface of the catalyst to the boundary layer surrounding the catalyst, there is no chemical change in this process.

2. Internal pore diffusion is the diffusion of reactants A outer surface of the catalyst into catalyst pore. Since catalyst pore have variable size and shape, there is collision in this stage both between reactant A and wall of porous.

3. Adsorption is the adsorption of reactant A on outer surface of catalyst and here are chemical changes in this stage. Catalysis always occur with chemical sorption by chemical bonding between reactant A molecules

which called adsorbate and outer surface of solid catalyst which called adsorbent. The adsorption resulting in the binding of the substrate as a single layer on catalyst surface.

4. Surface reaction, in this stage the reaction occurs at the surface of the catalyst. The reaction of A into B at active site.

5. Desorption, in this stage B molecule desorb or detach from catalyst surface after the reaction are terminated as the final step of chemical reaction.

6. Diffusion of product from catalyst porous to the outer surface of catalyst. If the reaction in 4th stage is incomplete, reactant A also diffuse.

7. Diffusion of product B from outer surface of catalyst to the boundary later surrounding catalyst and fluid stream. If the reaction in 4th stage is incomplete, reactant A also diffuse.
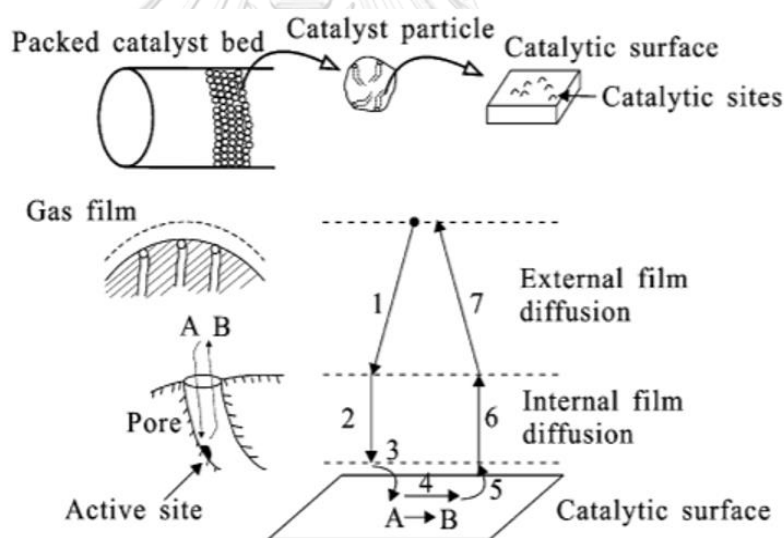
Fig. 2.3 Steps in heterogeneous catalysis reaction A → B in a porous supported catalyst [38].

2.6 Physical properties of catalyst

The physical properties of catalyst are surface area, pore volume, pore size and pore size distribution.

Surface area of catalyst is very important since surface area is proportional to the catalytic ability. There are active sites resulting from the combination of atoms and

molecules on metal surface. Surface area of catalyst can be determined by BET technique which base on inert gas adsorption such as liquid nitrogen gas on catalyst surface. However, this method is quite difficult. Therefore, the best way to increase the surface area of the material is to create many small pores.

Size and number of pores can indicate the amount of surface area within the catalyst. The catalyst with high internal surface area has very dense small pores which result in high dispersion of active site. Pore size in the reaction must be appropriate to precursors and products. It can take the most advantage of active site since pore size is critical to catalytic ability. Pore sizes can be divided into 3 types as:

1. Macropores: Pore size is larger than 50 nm or average pore radius is larger than 25 nm.

2. Mesopores: Pore size is between 2 – 50 nm or average pore radius is between 1 – 25 nm.

3. Micropores or atomic pores: Pore size is smaller than 2 nm or average pore radius is less than 1 nm

2.7 Metal oxides Catalyst [39]

Among the different fields of heterogeneous catalysis, catalysis by metal oxides is one of the most important, as it covers the majority of processes and of catalyst families used industrially, such as silica, alumina, clays, zeolites, SiO_2, MgO, CaO, TiO_2, ZnO, ZrO_2, porous and mesoporous metal oxides. Metal oxides such as MgO, Al_2O_3 and SiO_2 are often used as supports for metals because of their high stability and inactivity and are also used in dehydration and isomerisation reactions. Zeolites are important catalysts for the catalytic cracking of petroleum fractions to C_2-C_{14} hydrocarbons

2.8 Fly ash application

Fly ash is a waste from of coal combustion in the power plants. The disposal of coal fly ash requires enormous empty land, which can be used to dump the ash. Ash dams that bring environmental problems, such as air pollution and groundwater contamination, due to the leaching of metals from the ashes, especially the accumulation of the very fine particles of fly ash. Therefore, the management of fly ash

produced by coal fired power plants is considered to be a major problem. Fly ash contains 30–60% SiO_2, 10–30% Al_2O_3, 5–10% Fe_2O_3, 5–10% MgO and 2–4% CaO in it. The majority of fly ash content consisted of quartz, mullite, hematite and magnetite [40]. To date, fly ash has found only low end uses such as an additive in cement. In addition, It was found used to neutralize and reduce sulphate content of acid and circumneutral mine waters [41, 42] However, fly ash consisted of the high Al and Si content, they can be converted to raw material for the synthesis of high value zeolites [43]. The effective utilization of fly ash as a catalyst would not only improve problem of environment but also helps in importance addition with a low-cost alternative source.

2.9 Oil quality analysis [44, 45]

The analysis of oil quality determines the composition and properties of crude oil by oil refining based on boiling range, which divided into a small range of   5–10 °C. However, oil refining based on boiling range is not popular due to high cost and time consuming. Currently, oil refining is done by dividing into wide boiling point range that suitable for application. The boiling range can be divided into:

1. Initial boiling point (IBP) to 200 °C for gasoline fraction which used in gasoline production.

2. Boiling point between 200 – 250 °C for kerosene fraction which used as lamp oil providing illumination. High quality kerosene oil has no smoke. However, if the freezing point is low it can be used as jet aircraft fuel and depending on other properties of fuel.

3. Boiling point between 250 – 350 °C for light gas oil which used as engine oil.

4. Boiling point between 350 – 370 °C for gas oil fraction which used as diesel engine fuel.

5. Boiling point above 370 °C for high molecular weight residue which can be used in many applications depending on the properties of waste oil such as fuel oil, asphalt or lubricant.

2.10 Literature Reviews

Over the years, numerous researches regarding catalytic cracking with various substrates successfully produce commercial fuels and standard fossil fuels. The substrates can be vegetables, fish, meals, triolein, and triglycerides. To illustrate, N. Asikin-Mijan et al. [46] study on catalytic cracking of triolein and their research accomplishes on producing commercial fuels. They prove that the catalyst clamshell-derived CaO-based, it can removed oxygen from carboxyl group of fatty acid or oil in the form of CO_2 and CO via decarboxylation or decarbonylation reaction, respectively. H. Seifi and S.M. Sadrameli [47] investigate catalytic cracking of triglycerides and their methyl esters for improvement of renewable transportation fuel. They found that the liquid product from catalytic cracking can improved fuel properties such as viscosity, curve, heating value and acid number and make the renewable fuel very similar to the commercial fuels. Erick Yuki Emori et al. [48] investigate the catalytic cracking process of soybean oil using ZSM-5 zeolite. They used catalyst is commercial zeolite ZSM-5 with Si/Al molar ratio of 20. The experiment carries out in micro fixed-bed reactor and add refined soybean oil is pumped at 0.07 g/min with gas flow rate of 42 ml/min at 723 K for 45 min. It can be concluded that ZSM-5 catalyst, produced more liquid fuel under H_2flow than under N_2flow. The highest amount of gasoline is produced with refined oil under H_2 flow, while the selectivity lower, the result indicates that the oxygenated content is higher. Zerihun Demrew Yigezu and Karuppan Muthukumar [49] study catalytic cracking of vegetable oil with metal oxides for biofuel. They investigate the physical and chemical properties of the products and influence the variables on the product, six different metal oxides (Co_3O_4, KOH, MoO_3, NiO, V_2O_5, and ZnO) are used as catalysts. The maximum conversion (87.6%) is obtained with V_2O_5 at 320 ˚C in 40 min, whereas, the minimum conversion (55.1%) is obtained with MoO3 at 390 ˚C in 30 min. The physical characteristics of the product obtained (density, specific gravity, higher heat value, flash point and kinematic viscosity), are investigated according to ASTM D6751 (B100) standards, which mainly hydrocarbons consisted of methyl and ethyl esters. Furthermore, the liquid fuel obtained are distilled and separated into four components, which are light hydrocarbons, gasoline, kerosene and heavy oil, the value

are 18.73%, 33.62%, 24.91% and 90.93%, respectively. Dan Cheng et al. [50] study catalytic cracking of crude bio-oil from glycerol-assisted liquefaction of swine manure using a modified zeolite catalyst. They investigate the effects of cracking temperature, reaction time and catalyst loading. After cracking the yield and quality of oil are analyzed. The result showed the yield of upgrading bio-oil decreased when an increase of temperature, reaction time and catalyst loading, but the viscosity, heating value and composition of the upgraded bio-oil became more desired. In addition, the information from GC–MS show the increased cracking of long-chain acid methyl esters creating several alkanes, alkenes and their isomers, and short-chain acid methyl esters. It can be concluded that the temperature and high catalyst loading improved the selectivity of cracking long chain acid methyl esters to alkanes and alkenes. A.A. Mancio et al. [51] investigate catalytic cracking of crude palm oil at pilot scale using Na_2CO_3 as a catalyst for produce biofuels. The effect of catalyst content, yield and chemical composition of liquid product is considered at a pilot scale. The experiments carried out in a reactor of 143 L at 450∘C and 1 atm, using 5%, 10%, 15%, and 20% (w/w) Na_2CO_3 as the catalyst. The increasing catalyst content, the kinematic viscosity of oil reduce from 6.59 to 3.63 mm_2s^{-1} and the acid value decreases from 51.56 to 1.26 mg KOH/g. The GC–MS show that comprise and oxygenated compounds, when increase catalyst content, the concentration of hydrocarbons increase, while the concentration of oxygenates decrease. M.J.A. Romero et al.[52] study deoxygenation of waste cooking oil and non-edible oil to produce of liquid hydrocarbon biofuels, carried out in batch and semi-batch experiments using CaO as catalysts. The result show that waste cooking and non-edible oil are positively deoxygenated and can convert to hydrocarbon biofuels. Moreover, the liquid fuel include high hydrocarbon composition and low sulfur content similarly to diesel fuel, it can be used for engines and transportation. Moreover, Nadia Mrad et al. [53] investigate catalytic cracking of fish oil industrial to produce Liquid hydrocarbon fuels. The variables include temperature, type of catalyst and the heating rate on the yield of liquid oil and acid value. Condition in the experiment is obtained in a temperature range of 300–500˚C, heating rate of 10 ˚C/min and using a mixture of Al_2O_3 and Na_2CO_3 as a catalyst, give the highest yield of biofuel at 72% wt. Additionally, the result show that the mixture of Na_2CO_3 and

MgSO$_4$ as a catalyst give lowest acid value of 8.75 mgKOH/goil and 68.1% of OLF yield.

Although the catalytic cracking procedure can be applied to various substrates, this study uses coal fly ash. There are two main reasons as follows: 1) a low cost of catalyst and 2) the composition of several metal oxides. Due to the low cost of coal fly ash, some studies use it in the cracking method, for example, N. Muthukumaran et al. [54] study catalytic cracking Calophyllum inophyllum oil using fly ash catalyst for produce diesel engine fuel. The result of this research show drops in engine performance and combustion for increase oil blends, although the emissions were detected in engine to be low. S. Prasanna Raj Yadav et al. [55] investigate catalytic cracking of waste transformer oil to liquid fuel using fly ash catalyst. The objective of this research is to decrease the environmental problems from landfill, so they indicate fly ash as a catalyst in the experiment. The result indicated that transformer oil, it cracks to smaller hydrocarbon groups, moreover physical and thermal properties of liquid fuel are initiating to be in commercial fuel. Furthermore, Deepti Jain et al. [56] study using fly ash as a material for Synthesis and characterization of novel solid base catalyst. The result shows the increase of amorphous properties in solid base fly ash is likewise regular crystalline shape of zeolites particles confirmed by XRD data. Not only that, but also the improved BET surface area in solid base fly ash seriously rises the reaction capacity and growths the selectivity of the product.

Additionally, many researchers have studied about kinetics study of catalytic cracking as follows: Samia A. Hanafi et al. [57] investigate kinetic study of hydrocracking of waste chicken fat for renewable fuel production in a fixed bed reactor. In this study use NiW/SiO$_2$–Al$_2$O$_3$ as a catalyst. The liquid fuel is examined using distillate gas chromatography (ASTM D-2887), the results indicate that liquid product from catalytic cracking have a physico-chemical properties similarly to petroleum fuels. The kinetics study shows the second order and activation energy is 96 kJ mol^{-1}. Desavath V. Naik et al. [58] examine a 5-lump kinetic model is proposed and validated to mean the catalytic cracking of pyrolysis oils with equilibrium fluid catalytic cracking catalyst. The estimate the kinetic parameter use data from experimental and a 5-lump model is used to represent the yields of gasoline, LPG, dry

gases, coke and feed stocks. Moreover, Kai Xiong et al. [59] prove kinetics study of catalytic cracking of heavy oil over an in-situ crystallized FCC catalyst. The kinetic parameters are estimated based on experimental data at 460, 480, 500 and 520 ˚C by fourth order Runge–Kutta algorithm and the least square method. Frequency factors and apparent activation energies are calculated according to Arrhenius equation. The predicted data of product distribution showed good agreement, model analysis indicated that a relatively low temperature is more suitable to produce light oil.

CHAPTER 3
MATERIALS AND METHODS

The waste chicken fat is mainly constituted of triglycerides that can be used as feedstock for biofuel production. In this study, waste chicken fat from the food industry and fly ash from a power plant was used as raw materials for the catalytic cracking process. The experiment was set up at the center of fuels and energy from biomass, Saraburi, Thailand.

3.1 Batch experiment

This research was conducted on the factors that influence the catalytic cracking reaction of waste chicken fat to liquid fuel on fly ash catalysts in a batch reactor by determining the optimum conditions of the catalytic cracking in batch reactor. To obtain the maximum yield of liquid fuel with the appropriate composition, the batch reactor was investigated for the kinetic pathway of catalytic cracking.

3.1.1 Instruments

1. A stainless-steel micro-reactor of 70 mL as a batch reactor. The top of the reactor is covered by a stainless-steel lid with a gas compressor device and a safety valve. The experiment conditions were done for the temperature of 500 °C and at a pressure of 10 kPa. A thermocouple slot for measuring the temperature was placed inside the reactor during the experiment.

Fig. 3.1 Batch reactor (70 ml)

2. A temperature controller, which is used to control the power supply from transformer to heating coils and to stop the power supply when the required temperature is obtained. It can control the temperature at $\pm$ 10 $^{\circ}$C.

3. An injection heating coil with a voltage of 230 volts and a power of 400 watts.

4. A k-type thermocouple for measuring temperature with 1.6 mm diameter.

5. A reactor controller device with a motor to drive the spindle which can be adjusted to the speed as shown in Fig. 3.2 (a)&(b)
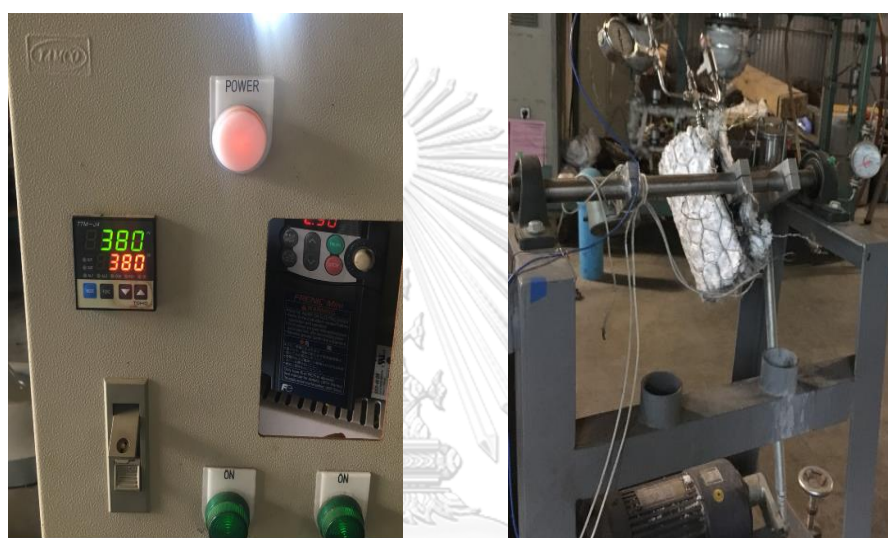
Fig. 3.2 *(a)* Digital temperature controller *(b)* Reactor.

6. A vacuum filter unit, which consists of a glass container connected to a suction machine, in order to filter and separate liquid product from solid residue using a glass filter.

7. A two decimal places scale of analytical balance

8. A four decimal places scale of analytical balance

9. A stopwatch

10. An oven

11. Glassware (beaker, bottle samples)

12. Gas Chromatography and simulated distillation software from Agilent Technologies model GC7890A for analysis of the composition of liquid fuel products by periodic boiling point according to ASTM D2887 standard as shown in Fig. 3.3.
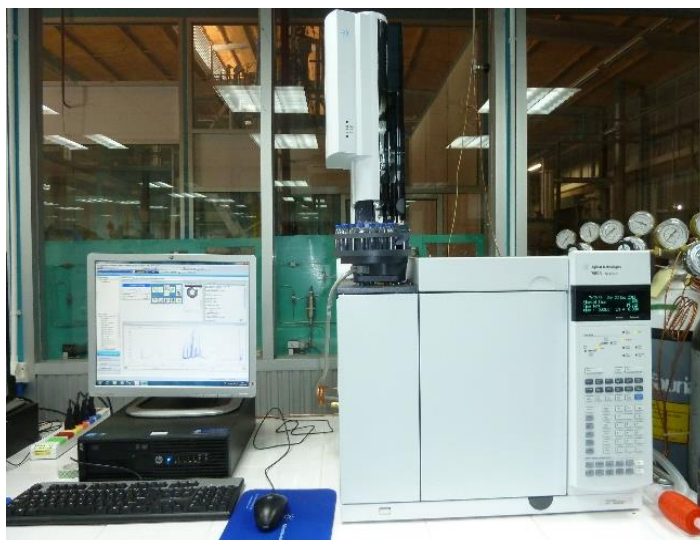
Fig. 3.3 Gas Chromatography and simulated distillation software.

13. Gas Chromatography – Mass spectrometer (GC-MS): Gas Chromatography model GC2010 that use Mass Spectrometer model GCMSQP2010 as a detector from Agilent. The analysis was done on 0.25 mm. x 30 m. Capillary column from J&W Scientific model DB-1 with 100% dimethylpolysiloxan, film thickness 0.25 μm as stationary phase and the operation temperature range of this unit is from -60 to 350°°C as shown in Fig. 3.4.

Fig. 3.4 Gas chromatography – mass spectrometer, GC-MS.

14. Surface area and porosity analyser for analysis of surface area and porosity of catalyst by measuring nitrogen that was adsorbed on sample surface. Then the BET equation is used to calculate the specific surface area. Simulated distillation gas chromatography is shown in Fig. 3.5.

Fig. 3.5 Micrometrics ASAP 2020 Physisorption BET.

15. X-Ray Fluorescence Spectrometer (XRF) as shown in Fig. 3.6 was used for analysis of composition of catalyst. XRF technique relied on specific photo emission of substance which has specific wavelength for element. Therefor it can indicate the elements that are present in the sample.

Fig. 3.6 X-Ray Fluorescence Spectrometer.

16. X-ray diffraction spectroscopy (XRD) X- ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays diffracted at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the X-ray diffraction pattern is the fingerprint of the periodic atomic arrangements in a given material. The crystalline phase com-position of fly ash catalyst was analysed by XRD.
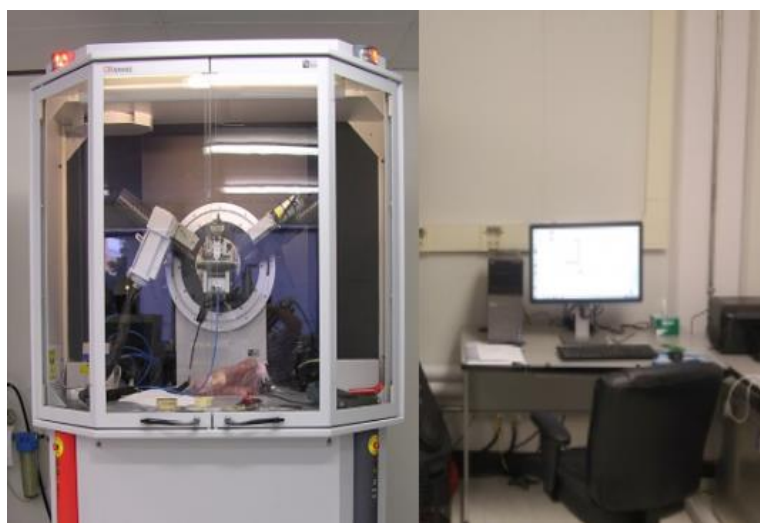
Fig. 3.7 X-ray diffraction spectroscopy.

3.1.2 Reagent and chemical

- The waste chicken fat investigated in this study was provided by chicken processing plant located in Nontaburi province. Fig 3.8 illustrated waste chicken fat

Fig. 3.8 Waste chicken fat.

- 99.99% of hydrogen gas was contained in 6 L high pressure tank.
- Waste fly ash produced from the coal fired power plants in Rayong province
- Hydrogen gas (purity 99.5%) used to trace the effect of initial pressure of hydrogen gas
- Toluene (C_7H_8) is a commercial grade (purity 80% minimum) from S.R.Lab Co., Ltd. Bangkok, Thailand. This reagent was used without further purification.

3.1.3 Catalyst Preparation

The coal fly ash generated from power plant industry in this work is a reusable catalyst to reduce the total fuel cost and came up with an idea of utilizing waste coal fly ash as a catalyst for the catalytic cracking process. The mixture of fly ash was heated at in 600 ˚C for 1 hour to remove large impurities shown in fig 3.9. X-ray fluorescence techniques have been used to characterize a coal fly ash catalyst.
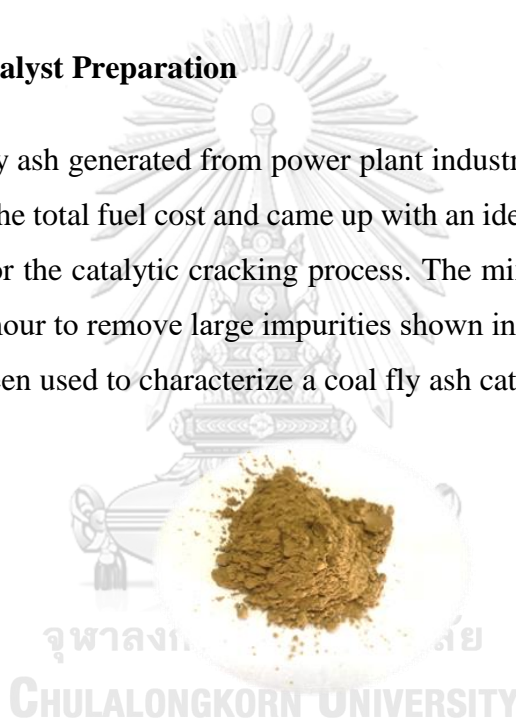
Fig. 3.9 Coal fly ash was heated at in 600 ˚C for 1 hour.

3.1.4 Experimental analysis

1. Characterizing the primary properties of waste chicken fat including the physical properties, decomposition temperature range, chemical composition, fatty acid composition, the boiling point range and the ultimate analysis. Mass spectrometry was used to determine the profile of waste chicken fat.

2. Characterizing the primary properties of catalyst including composition of coal fly ash catalyst by XRF and determine surface area of catalyst by BET.

3. 2-level factorial designs are used to study the influence of various variables affecting on the percentage of liquid product from catalytic cracking of waste chicken fat on fly ash catalyst by using 2^4 factorial experimental design. The studied variables are reaction temperature, reaction time, catalyst content and initial hydrogen pressure as shown in Table 3.1 and 3.2.

4. Analyze the physical and chemical properties of liquid product from experiment and determine the quantity of solid, liquid and gas product in term of weight percent.

Table 3.1 The studied variables parameter.

Variables	Level	
	Low (-)	High (+)
Temperature (°C) , A	420	450
Time of reaction (min) , B	45	75
Mass of catalyst (% wt), C	1	5
Initial hydrogen pressure (Bar), D	1	5

Table 3.2 Number of trials from 2-level factorial experimental design.

Variables			
Temperature (°C), A	Time of reaction (min) , B	Catalyst content (% wt), C	Initial hydrogen pressure (Bar), D
460	75	5	5
440	60	3	3
420	75	1	5
460	75	5	1
460	45	1	1
440	60	3	3
460	45	5	1
460	75	1	1
420	45	1	5
460	75	1	5
420	45	1	1
420	45	5	5
420	75	1	1
420	75	5	5
420	45	5	1

440	60	3	3
440	60	3	3
440	60	3	3
420	75	5	1
460	45	1	5
460	45	5	5

3.1.5 Experimental methodology

1. The waste chicken fat (15 g) was filled to a reactor with analytical balance (0.01 readability). The catalyst (1,3,5 wt.% fly ash as catalyst) was placed into reactor by four decimal points of analytical balance.

2. Purging air inside the reactor by flushing hydrogen for three times then compress hydrogen gas was set up at 1 bar. Since the reactor had a small volume of only 70 mL and hydrogen gas was not the main reactant so there is no need to calculate the amount of hydrogen required by the waste chicken fat.

3. Purging air inside the reactor by slowly passing hydrogen gas then compress hydrogen gas to the given pressure (in case setting up high pressure of hydrogen) by observing the pressure from the regulator connected between the hydrogen tank and reactor. Checking for gas leak at the joints of the reactor if there is no gas leak, slowly closing gas valve in order to prevent gas coming out.

4. The reactor was heated by external electric resistance. The temperature was measured and controlled by a thermocouple inserted inside the reactor. Then putting the insulation around the reactor to prevent heat loss during the experiment. Turning on the temperature controller unit, setting up the reaction temperature and recording the reaction time after reaching the required reaction temperature.

5. After finishing the reaction time, removing insulator and heating coil and the reactor was cooled down close to the room temperature. Then, slowly venting gas outside the reactor (if the gas is vented when the reactor temperature is not close to room temperature, some of the gaseous cannot condensed which will resulted in the error experimental).

6. Opening the lid of reactor, recording the reactor weight after the experiment in order to calculate gas content by using equation (3.1).

Gas content = reactor weight before the experiment start

$$\qquad\qquad\text{- reactor weight after the experiment finish} \qquad (3.1)$$

     7. Separating liquid from solid by using vacuum filtration unit. The reactor is wiped clean by cleaning paper that was pre-dried and weighted in order to reduce the error of the calculated results. After solid and cleaning paper are wrapped with foil that was pre-dried and weighted. Then drying in the oven at 110°C for 24 h, weighing and calculating the solid content by using the equation (3.2).

Solid content = weight of filter paper, foil and solid residue after drying

$$\qquad\qquad\text{- weight of filter paper, foil before using filtration} \qquad (3.2)$$

     8. Calculating the amount of liquid product from equation (3.3).

Liquid product content = weight of waste chicken fat

$$\qquad\qquad\text{- weight of gas – weight of solid} \qquad (3.3)$$

     9. Analyses liquid product by Simulated Distillation Gas Chromatography to determine the distribution of compositions of liquid product in various periodic boiling points and studying physical and chemical properties of the obtained liquid product.

     10. Calculating the percentage of liquid product

$$\% \text{ liquid yield} = \frac{\text{weight of liquid product} \times 100}{\text{weight of original oil}}$$

     11. Analyses experimental results and concluding the optimum condition of catalytic cracking of waste chicken fat.

3.2 Continuous experiment

The purposes of this work studies the factors that affect the catalytic cracking reaction of waste chicken fat in the continuous reactor to liquid fuel using coal fly ash catalysts and determining the optimum conditions in continuous reactor in order to achieve the maximum yield of liquid fuel.

3.2.1 Instruments

1. Catalytic cracking experiments were carried out in a horizontal continuous reactor described in Fig. 3.10 with a 316 stainless steel reactor, giving a volume of 3 L. The reactor was heated via an electrical furnace controlled by a temperature controller. The temperatures were monitored using thermocouple inserted in the reactor.

Fig. 3.10 3 L-Continuous-flow reactor.

2. Digital temperature controller is used to control the power distribution from transformer to heating coils in various parts of the reactor and stop the power distribution when the required temperature is obtained. Temperature control can be divided into 3 parts:

- Controlling temperature inside the reactor
- Controlling temperature of gaskets on both sides
- Controlling temperature of carrier gas

as well as the screen that display temperature inside the reactor as shown in Fig. 3.11.

Fig. 3.11 Digital temperature controller.

3. Putting heating coil, 230 V and 400 W for heating the reactor.

4. K-type thermocouple with 1.6 mm diameter for measuring the temperature of obtained product and reaction temperature of catalysts were set up.

5. Carrier gas, nitrogen gas is used as carrier gas to carry rapidly the obtained product vapour to the condenser. There are 2 gas feed controller:

- Carrier gas feed controller at gaskets on both sides

- Carrier gas feed controller in reactor

6. Condenser unit consist of: as shown in Fig. 3.12

- (a) Counter-current heat exchanger

- (b) Cooling tower
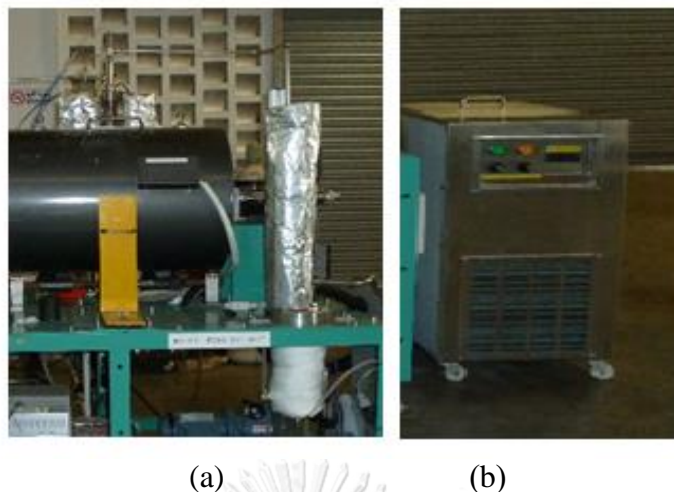
(a)   (b)

Fig. 3.12 Condenser Unit.

7. Vacuum filter unit consists of glass container connected to vacuum pump using to filter and separate liquid product from solid residue using filter paper.

8. Analytical balance 0.01 readability specification

9. Analytical balance 0.0001 readability specification

10. Stopwatch

11. Oven

12. Glassware (beaker, bottle samples)

13. Gas Chromatography and simulated distillation for analysis of the composition of liquid fuel products by boiling point as shown in Fig. 3.13.

Fig. 3.13 Simulated distillation gas chromatography.

14. Gas Chromatography– Mass spectrometer (GC-MS): Gas Chromatography model GC2010 that use Mass Spectrometer model GCMSQP2010 as a detector from Agilent. The analysis was done on 0.25 mm. x 30 m. Capillary column from J&W Scientific model DB-1 with 100% dimethylpolysiloxane, film thickness 0.25 μm. as stationary phase and the operation temperature range of this unit is from -60 to 350°C as shown in Fig. 3.14.

Fig. 3.14 Gas chromatography – mass spectrometer, GC-MS.

3.2.2 Reagent and chemical

- The waste chicken fat in this study was provided by chicken processing plant located in Nonthaburi province.
- 99.99% Nitrogen gas contained in 6 L high pressure tank.
- Waste fly ash produced from the coal fired power plants in Rayong province.

3.2.3 Experiment

2-Level experimental design are used to study the influence of variables affecting on percentage of liquid product from catalytic cracking of waste chicken fat on fly ash catalyst by using 2^4 factorial experimental design. The studied variables are reaction temperature, feeding rate, N_2 gas flow rate and catalyst content as shown in Table 3.3.

Table 3.3 The studied variables in catalytic cracking of waste chicken fat on fly ash catalyst.

Variables	Level	
	Low (-)	High (+)
Reaction temperature ($^{\circ}$C) , A	420	460
Feeding rate (ml/min), B	3	9
N_2 gas flow rate (ml/min), C	50	150
Catalyst content (% V/V), D	30	60

Table 3.4 Number of trials from 2-level factorial experimental design.

Variables			
Temperature ($^{\circ}$C), A	Feeding rate (ml/min), B	N_2 gas flow rate (ml/min), C	Catalyst content (% V/V), D
460	3	150	60
460	3	50	60
460	9	150	30
440	6	100	45
460	9	50	30
420	3	50	60
440	6	100	45
420	9	50	30
460	3	150	30
460	9	150	60
420	9	50	60
420	3	150	30
420	3	150	60
420	9	150	30
460	9	50	60
460	3	50	30
440	6	100	45
420	3	50	30
420	9	150	60
440	6	100	45
440	6	100	45

3.2.4. Research methodology

1. Weighing waste chicken fat is before fed to the reactor using 0.01 readability and fly ash catalyst is also weighted to the desired amount using 0.0001 readability.

2. Connecting the reactor to the controller, heating unit and cover the insulator in order to prevent heat loss during the experimentation. Then thermocouple was placed insert in to the reactor.

3. Adding fly ash catalyst to continuous reactor and cover with the lid.

4. Turning on the stirrer and feeding carrier gas at the desired rate by setting the controller. Adjusting an electric current from the screen to distribute power into heating coil and wait until reaching the required temperature.

5. Starting time when temperature inside the reactor reaches to the desired temperature. Collecting the product, separate the liquid product from solid residues by vacuum filtration using glass filter and the separate liquid was used for further analysis.

6. Washing the reactor with toluene solution, wipe clean with pre-weighted soft paper. The solid product and soft paper are dried in oven at 105°C for 24 h, weight and calculate the overall yield.

7. The liquid product is analysed with Simulated Distillation Gas Chromatography to determine the compositions distribution of liquid product in various periodic boiling points and chemical compositions.

8. Calculating the percentage of liquid product.

Percentage of liquid product = $\dfrac{\text{mass of liquid product}}{\text{mass of fed waste chicken fat}} \times 100$

CHAPTER 4
RESULTS AND DISCUSSIONS

This research concentrates on catalytic cracking of waste chicken fat by using waste fly ash catalyst for synthesize liquid fuel product, mainly focuses on naphtha and diesel, with value added compositions. The reason why this study targets on naphtha and diesel is because these two products can be used as commercial fuels. The cracking processing is a complex reaction, therefore, the kinetics of catalytic cracking is essential investigated. Under the concentrated procedure in batch reactor, this method studies on the effect on liquid fuel product, which varies according to temperature, time, catalyst content, and initial hydrogen pressure; and the optimum condition of maximum of liquid product.

4.1. Properties of waste chicken fat

In this research, waste chicken fat is used as raw material. The waste chicken fat properties must be investigated before using and after cracking in order to comparison on its characteristics, which will be explained in 4.4, both in chemical composition and chemical properties.

4.1.1 The fuel composition of waste chicken fat

Table 4.1 is shown the fraction of distillation ranges by boiling points of fuel composition, which has naphtha, kerosene, diesel and long residue. Fuel composition of waste chicken fat is analyzed according to American Society for Testing and Materials (ASTM) by using Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, ASTM D2887. It is observed that waste chicken fat consisted of four main compositions: 10% naphtha, 9 % kerosene, 21 % diesel (light gas oil and gas oil) and 60 % residue by weight. It can be observed that fuel composition waste chicken fat mainly consisted of high content of long residue. It is not suitable to be directly used as fuel. Therefore, it is interesting to change the large hydrocarbon molecules into smaller hydrocarbon molecules by catalytic cracking and produced liquid fuels with properties similar with petroleum fuel.

Table 4.1 The composition of waste chicken fat.

Boiling Point(°C)	Composition	%wt
IBP - 200	Naphtha (C_5-C_{12})	10.00
200 - 250	Kerosene (C_{12}-C_{15})	9.00
250 - 350	Light gas oil (C_{15} - C_{25})	15.00
350 - 370	Gas oil (C_{25} - C_{33})	6.00
370 - FBP	Long Residue (>C33)	60.00

4.1.2 The chemical composition of waste chicken fat

Chemical composition of waste chicken fat is studied by using gas chromatography-mass spectrometry as shown in Fig. 4.1 which showed the chromatogram of waste chicken fat composition. Two dominant peaks are found n-hexadecanoic acid (C16) and 9-Octadecenoic acid (C18) as shown in Table 4.2 at 9.956 min. and 10.822 min., respectively.
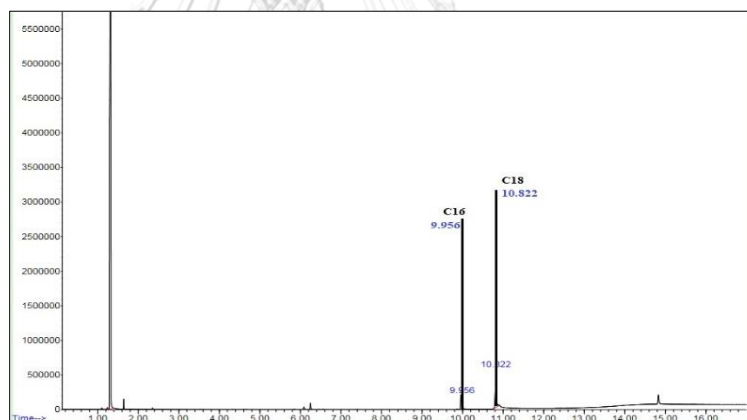
Fig. 4.1 The chromatogram of waste chicken fat by GC-MS.

Table 4.2 The chemical composition of waste chicken fat by GC-MS.

Retention time (min)	Compounds	Formula	Area (%)
9.956	n-Hexadecanoic acid (Palmitic acid)	$C_{16}H_{32}O_2$	21.81
10.822	9-Octadecenoic acid (Oleic acid)	$C_{18}H_{34}O_2$ or $C_8H_{17}CH=CH(CH_2)_7COOH$	66.81

In the fatty acid profile of waste chicken fat contains 27.95 % saturated fatty acid and 70.45 % unsaturated fatty acid, that consisted of 21.62 % Palmitic acid

(C16:0), 34.48 % Cis-9-Octadecenoic acid (C18:1 n-9) and 25.11% Cis-9, 12-Octadecadienoic acid (C18:2 n-6) as shown in Table 4.3. According to this information, the waste chicken fat is suitable for producing liquid fuel by catalytic cracking process due to the high contain of long chain hydrocarbons. Afterward, the long chain hydrocarbons can be decomposed into a medium chain.

Table 4.3 The composition of fatty acid in waste chicken fat.

Fatty acid composition	Wt. %
Lauric acid (C12:0)	0.47
Myristic acid (C14:0)	0.74
Pentadecanoic acid (C15:0)	0.11
Palmitic acid (C16:0)	21.62
Heptadecanoic acid (C17:0)	0.12
Stearic acid (C18:0)	4.73
Arachidic acid(C20:0)	0.10
Behenic acid (C22:0)	0.02
Lignoceric acid (C24:0)	0.04
Total saturated fatty acid	**27.95**
Myristoleic acid(C14:1)	0.14
Palmitelaidic methyl ester (C16:1t9)	0.03
Palmitoleic acid (C16:1 n-7)	4.31
Cis-9-Octadecenoic acid (C18:1 n-9)	38.48
Cis-9,12-Octadecadienoic acid (C18:2 n-6)	25.11
Cis-9,12,15-Octadecatrienoic acid)C18:3 n-3)	1.64
Cis-11-Eicosenoic acid (C20:1 n-9)	0.34
Cis-11,14-Eicosadienoic acid (C20:2 n-6)	0.19
Cis-5,8,11,14-Eicasatetraenic acid (C20:4 n-6)	0.17
Cis-5,8,11,14,17-Eicosapentaenoic acid (C20:5 n-3)	0.02
Nervonic acid (C24:1)	0.02
Total unsaturated fatty acid	**70.45**
Unidentified peak	**1.60**

4.1.3 The ultimate analysis of waste chicken fat

The result of ultimate analysis of waste chicken fat has 4 element compositions, which are carbon, hydrogen, nitrogen, and oxygen which has 72.52 percentage, 10.17 percentage, 0.43 percentage, and 16.88 percentage of oxygen respectively as shown in Table 4.4. According to the high percentage of oxygen, it makes a heating value of waste chicken fat was lower than standard of commercial fuel. However, if waste chicken fat was cracked, which resulted in lower oxygen content and the obtained liquid product was more suitable to use as fuel.

Table 4.4 The element composition of waste chicken fat.

Elemental compositions of waste chicken fat (wt%)			
Carbon	Hydrogen	Nitrogen	Oxygen
72.52	10.17	0.43	16.88

4.1.4 The analysis of the range of thermal cracking temperature of waste Chicken fat by Thermo gravimetric Analyzer (TGA)

The thermo gravimetric analysis and DTG curves for thermal degradation of waste chicken fat in range of 50 – 600°C, the heating rate of 20°C/min under nitrogen atmosphere in Fig. 4.2. The decomposition takes place in three steps as follows: the first stage is mass loss of water and moisture in waste chicken fat. The next stage from 400.07- 456.7°C is a main decomposition of waste chicken fat, which occurs in this zone. In the final stage, the completely decomposition and devolatilization occur in this zone in the temperature between 500-600 °C, however, the waste chicken fat decompose at 436 °C. Basing on that fact, all experiments are carried on the temperature range of 420 - 460°C.
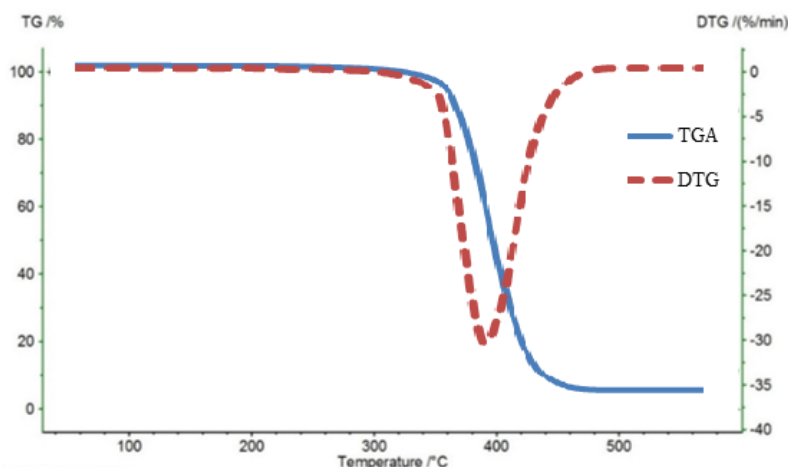
Fig. 4.2 The thermal decomposition range of waste chicken fat by TGA.

4.2 Properties of coal fly ash

4.2.1 The composition of coal fly ash

The ultimate analysis is performed by using energy dispersive x-ray spectrometer. The composition of coal fly ash illustrates in Table 4.5. It is found that SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO which potentially to using in catalytic cracking. The high contents of Si and Al could enhance the generation of hydroxyl radical and accelerate the catalytic cracking process. Moreover, MgO and CaO are efficient catalyst in decarboxylation and decarbonylation reaction.

Table 4.5 The elements of coal fly ash.

Chemical Composition (wt%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Coal fly ash	49.0	22.1	12.1	6.30	3.04

4.2.2 Surface area and pore volume of coal fly ash

The coal fly ash is calcination at 600°C for 1 hour to remove some impurities. The analysis of coal fly ash catalyst by N_2 physisorption measurement are presented in Table 4.6. Before calcination, the surface area is 1.80 m^2/g and the pore volume is 0.0094 cm^3/g. After calcination 600 ˚C, the surface area is 2.20 m^2/g and the pore volume is 0.0100 cm^3/g.

Table 4.6 Surface area and pore volume of fly ash in this work.

	Surface area and pore volume of fly ash catalyst	
	Before calcination	calcination 600 °C
Surface area (m^2/g)	1.80	2.20
Pore volume (cm^3/g)	0.0094	0.0100

4.3 The 2^k Experimental Design [60, 61]

The 2^k experimental design is an efficient method to evaluate how various reaction factors influence the system. It is very beneficial in the primary experimental study when there are several variables effects to determine. This study investigates variables affecting percentage of liquid product. The distribution of liquid product is the result from catalytic cracking of waste chicken fat using fly ash catalyst with 2^k factorial experimental design. The study of effects of variable on response will reduce the number of trials. Each variable can be divided into 2 levels, low and high level. This study focus on four variables, which are (a) reaction temperature, (b) catalyst content, (c) initial hydrogen pressure and (d) reaction time. The range and levels for each factor are showed below:

A : Temperature (°C), Low at 420°C (-) High at 460°C (+)

B : Reaction time (min), Low at 45 min (-) High at 75 min (+)

C : Catalyst content (%wt), Low at 1%wt (-) High at 5%wt (+)

D : Initial hydrogen pressure (bar), Low at 1 bar (-) High at 5 bar (+)

The above experimental design consists of 16 runs and adds with 4 replicate runs at center points which was reaction temperature (A) = 440°C, reaction time (B) = 60 min catalyst content (C) = 3 %wt. and initial hydrogen pressure (D) = 3 bar. There are totally 36 runs in the experiments.

4.3.1 The effect of variables on percentage of liquid product yield from catalytic cracking of waste chicken fat on fly ash catalyst.

2^4 factorial experimental design has an average value between 62.63 – 85.89 %wt. liquid products as shown in Table 4.7.

Table 4.7 Percentage of liquid product from catalytic cracking of waste chicken fat over coal fly ash catalyst.

Run	Factor A	Factor B	Factor C	Factor D	%yield of Liquid		Factor Level Low (-)	Factor Level High (+)
1	420	45	1	1	84.03	A (°C)	420	460
2	420	45	5	1	84.15	B (min)	45	75
3	420	45	5	5	85.20	C (%wt)	1	5
4	420	45	1	5	85.89	D (bar)	1	5
5	420	75	1	1	80.27			
6	420	75	1	5	84.63			
7	420	75	5	1	80.88			
8	420	75	5	5	80.54			
9	460	45	1	1	72.11			
10	460	45	1	5	64.76			
11	460	45	5	1	64.87			
12	460	45	5	5	69.50			
13	460	75	1	1	64.23			
14	460	75	1	5	63.23			
15	460	75	5	1	62.63			
16	460	75	5	5	66.10			
17	440	60	3	3	81.82			

The difference variables for the 2^4 design determines the half normal probability plot of liquid product yield as illustrated in fig. 4.3. From the half normal probability plot, all of the variables that lie along the straight line are insignificant, but the significant variables will deviate from the straight line. The parameter affects to liquid fuel product, which are temperature (A), reaction time (B), catalyst content (C) and initial hydrogen pressure (D) as summarized in Table 4.8. The analysis of each variable will discuss in section 4.5.
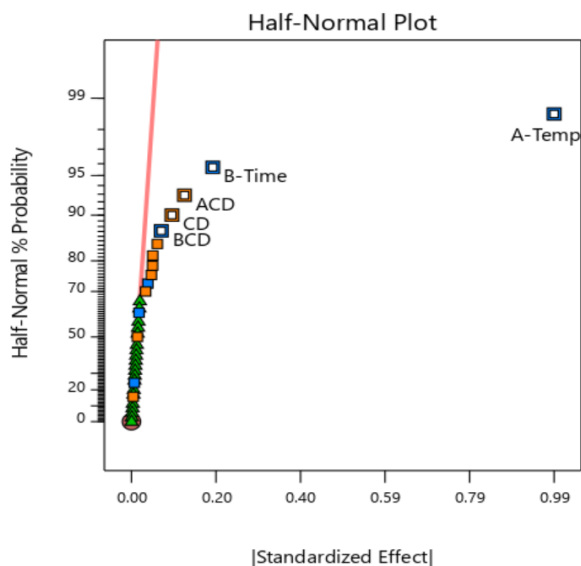
Fig. 4.3 Half normal probability plot of percentage of
liquid product yield in batch reactor.

Table 4.8 The variables influence on percentage of liquid product yield.

The variables influence on percentage of liquid product yield			
	One variable	Two variables	Three variables
Liquid	A, B	CD	ACD, BCD

  The analysis of variance (ANOVA) is selected the confidence interval of 95 percentages. The variables with the P-value less than 0.05 as shown in table 4.9. Residual analysis is necessary to confirm the assumptions for the ANOVA whether the data are reliable or not. If yes, Normal Plot of Residuals will be the straight line. The result of this research shows adjusted R^2 and predicted R^2 is 0.9763 and 0.9692, which is nearby 1 indicates that data are normally distributed as shown in fig 4.4. The optimum percentage of liquid yield is shown in equation 4.1.

Table 4.9 Analysis of Variance for 2^k experimental design in catalytic cracking of waste chicken fat on fly ash catalyst (liquid product yield).

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	p-value	
Model	2472.26	5	494.45	289.33	< 0.0001	significant
A-Temp	2322.55	1	2322.55	1359.03	< 0.0001	
B-Time	85.35	1	85.35	49.94	< 0.0001	
CD	18.70	1	18.70	10.94	0.0025	
ACD	33.83	1	33.83	19.79	0.0001	
BCD	11.83	1	11.83	6.92	0.0133	
Curvature	184.23	1	184.23	107.80	< 0.0001	
Residual	51.27	30	1.71			
Cor Total	2707.76	36				
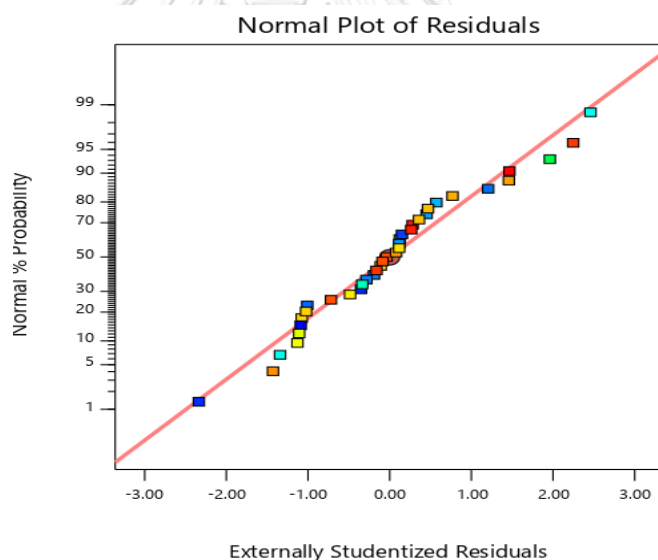
Fig. 4.4 The relationship between Normal % Probability and the residual of percentage of liquid product yield.

Percentage of liquid yield = $+237.67391-0.33318\times A-0.25059\times B$
$+10.87016\times C+13.92016\times D-0.031023\times A \times C$
$+0.038461\times A\times D+0.033865\times B\times C+0.043781\times B\times D$
$-4.85547\times C\times D+0.012852\times A\times C\times D$
$-0.010135\times B\times C\times D$ (4.1)

4.3.2 The effect of variables on percentage of naphtha yield from catalytic cracking of waste chicken fat using coal fly ash catalyst.

The average value of naphtha yield is between 15.00-32.00 %wt. by using 2^4 factorial experimental design as shown in Table 4.10.

Table 4.10 Yield of naphtha product from catalytic cracking of waste chicken fat over fly ash catalyst.

Run	Factor				%yield of naphtha		Factor Level	
	A	B	C	D			Low (-)	High (+)
1	420	45	1	1	16.00	A (ºC)	420	460
2	420	45	5	1	16.00	B (min)	45	75
3	420	45	5	5	15.00	C (%wt)	1	5
4	420	45	1	5	16.00	D (bar)	1	5
5	420	75	1	1	18.00			
6	420	75	1	5	17.00			
7	420	75	5	1	17.50			
8	420	75	5	5	18.00			
9	460	45	1	1	29.00			
10	460	45	1	5	29.50			
11	460	45	5	1	28.00			
12	460	45	5	5	26.00			
13	460	75	1	1	32.00			
14	460	75	1	5	30.00			
15	460	75	5	1	29.00			
16	460	75	5	5	28.50			
17	440	60	3	3	23.80			

The data from a factorial design is providing through examination of a normal probability plot. Fig 4.5 illustrates half normal probability plot of naphtha yield from the 2^4 design. The half normal probability plot are presented all of factor, but only the deviation from the straight line has significant parameters. The information in Table 4.11 presents the factor effect of naphtha yield from catalytic cracking of waste chicken fat on coal fly ash catalyst.
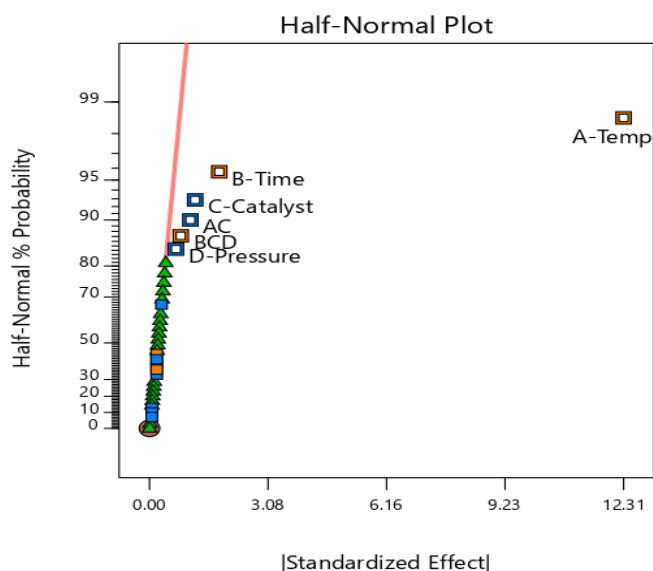
Fig. 4.5 Half normal probability plot of percentage of naphtha yield in batch reactor.

Table 4.11 The variables influence on percentage of naphtha yield.

The variables influence on percentage of naphtha yield			
	One variable	Two variables	Three variables
Naphtha	A, B, C, D	AC	BCD

The significant factors base on the F-value or P-value (probability value) with 95% confidence level. The analysis of variance (ANOVA) is examined the confidence interval of 95% or at of 0.05 significant interval. The larger F-value and the smaller P-value (Prob. > F), show more significant of the corresponding coefficient. Then, the variables with the P-value less than 0.05 are significant as presented in table 4.12.

A normal probability plot of residuals can be used to check the normality assumption. If the residuals plot approximates a straight line, then the normality assumption is satisfied. Fig. 4.6 finds that Residuals of percentage of naphtha yield should be straight line. Adjusted R^2 and Predicted R^2 is 0.9826 and 0.9764, respectively. The optimum percentage of naphtha yield is shown in equation 4.2.

Table 4.12 Analysis of Variance for 2^k experimental design in catalytic cracking of waste chicken fat on coal fly ash catalyst (naphtha yield).

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	p-value	
Model	1268.44	6	211.41	329.94	< 0.0001	significant
A-Temp	1212.78	1	1212.78	1892.80	< 0.0001	
B-Time	26.28	1	26.28	41.02	< 0.0001	
C-Catalyst	11.28	1	11.28	17.61	0.0002	
D-Pressure	3.78	1	3.78	5.90	0.0216	
AC	9.03	1	9.03	14.10	0.0008	
BCD	5.28	1	5.28	8.24	0.0076	
Curvature	3.95	1	3.95	6.17	0.0190	
Residual	18.58	29	0.6407			
Cor Total	1290.97	36				
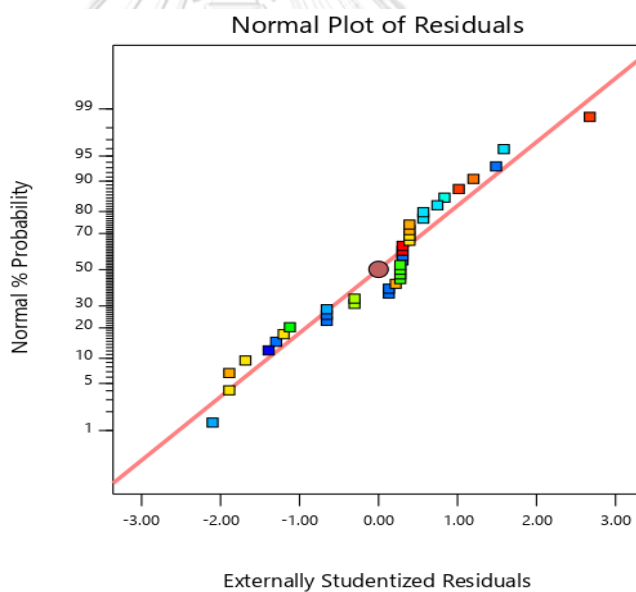
Fig. 4.6 The relationship between Normal % Probability and the residual of percentage of naphtha yield.

Percentage of naphtha yield = $-135.69531 + 0.34766 \times A + 0.11510 \times B$

$+1.13281 \times D - 0.013281 \times A \times C - 0.017188 \times B \times C$

$-0.021354 \times B \times D - 0.41406 \times C \times D$

$+0.006770 \times B \times C \times D$ (4.2)

4.3.3 The effect of variables on percentage of diesel yield from catalytic cracking of waste chicken fat on fly ash catalyst.

The percentage of diesel yield from catalytic cracking of waste chicken fat on the coal fly ash catalyst is shown in Table 4.13. It is found between 25.50-35.50 %wt. on percentage of diesel.

Table 4.13 Yield of diesel product from catalytic cracking of waste chicken fat using fly ash catalyst.

Run	Factor				%yield of diesel		Factor Level	
	A	B	C	D			Low (-)	High (+)
1	420	45	1	1	35.50	A (°C)	420	460
2	420	45	5	1	34.00	B (min)	45	75
3	420	45	5	5	35.00	C (%wt)	1	5
4	420	45	1	5	34.00	D (bar)	1	5
5	420	75	1	1	33.50			
6	420	75	1	5	33.50			
7	420	75	5	1	33.50			
8	420	75	5	5	32.50			
9	460	45	1	1	27.50			
10	460	45	1	5	27.50			
11	460	45	5	1	27.00			
12	460	45	5	5	27.50			
13	460	75	1	1	25.50			
14	460	75	1	5	26.50			
15	460	75	5	1	27.00			
16	460	75	5	5	27.00			
17	440	60	3	3	29.80			

A half normal probability plot of diesel yield in liquid fuels is presented in Fig.4.7. Half the normal probability plot indicates variables deviate from the straight line are significant terms. Therefore, the parameter influences on the percentage of diesel yield

from catalytic cracking of waste chicken fat on coal fly ash catalyst, which illustrated in Table 4.14.
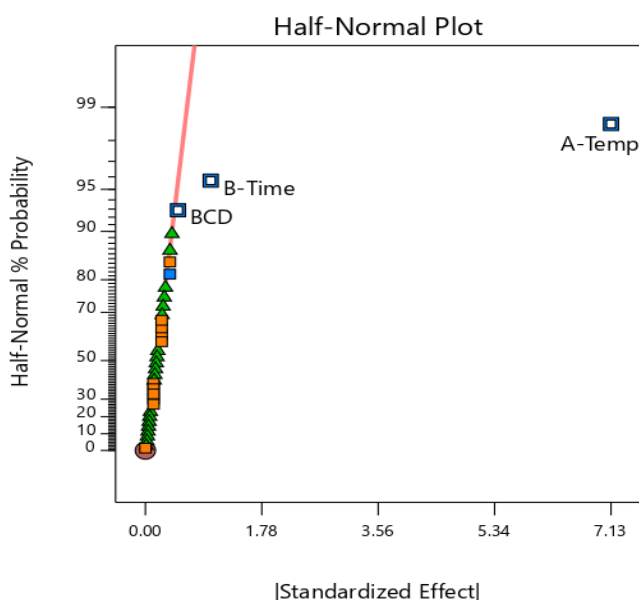
Fig. 4.7 Half normal probability plot of percentage of diesel yield in batch reactor.

Table 4.14 The variables influence on percentage of diesel yield.

| | The variables influence on percentage of diesel yield | | |
	One variable	Two variables	Three variable
Diesel	A, B	-	BCD

The adequacy of the model is justified by the analysis of variance (ANOVA). The analysis of variance is considered the confidence interval of 95% or at about 0.05 significant intervals. The ANOVA of catalytic cracking is given in Table 4.15, dividing the sum of the squares of each of the variation sources. The model and the error variance by the respective degrees of freedom and P-value less than 0.05 are considered as significant. The Normal Plot of Residuals as shown in the fig. 4.8, it is found the straight line of Residuals percentage of diesel yield. A high value of Adjusted R^2 and Predicted R^2 is 0.9627 and 0.9538, respectively. The optimum percentage of diesel yield is shown in equation 4.3.

Table 4.15 Analysis of Variance for 2^k experimental design in catalytic cracking of waste chicken fat on fly ash catalyst (diesel yield).

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	p-value	
Model	416.13	3	138.71	302.46	< 0.0001	significant
A-Temp	406.13	1	406.13	885.59	< 0.0001	
B-Time	8.00	1	8.00	17.44	0.0002	
BCD	2.00	1	2.00	4.36	0.0448	
Curvature	2.12	1	2.12	4.62	0.0393	
Residual	14.67	32	0.4586			
Cor Total	432.92	36				
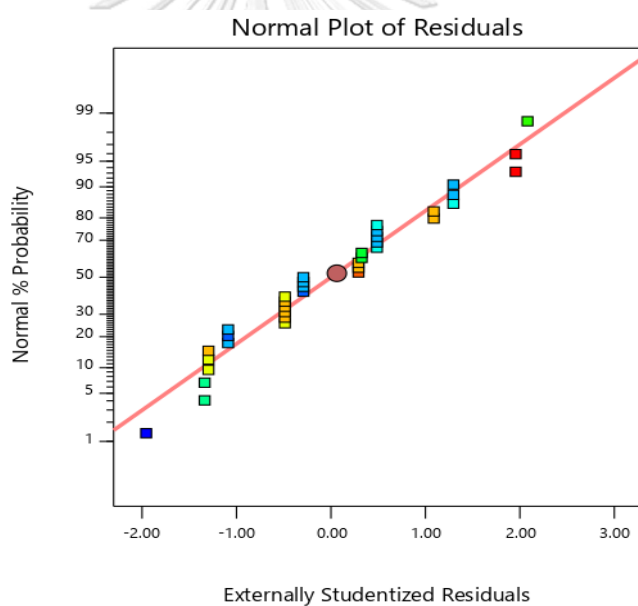
Fig. 4.8 The relationship between Normal % Probability and the residual of percentage of diesel yield.

Percentage of diesel yield = +114.71875-0.17813×A-0.095833×B

-1.18750×C -0.93750×D +0.018750×B×C

+0.014583×B×D+0.28125×C×D

-0.004166E ×B×C×D   (4.3)

4.4 The optimum condition of catalytic cracking of waste chicken fat on fly ash catalyst

Program of Design Expert version 11.0.0, which is software for the design of experiments, is used to analysis of the optimum condition. The ranges of variables in Table 4.16 shows the optimum condition. In this research, five responses are mainly considered as follows: percentage of gaseous product, percentage of solid, percentage of liquid product, percentage of naphtha yield and percentage of diesel yield. Gas and solid product are set in the lowest condition, whereas, the rest are set the highest condition. Afterward, Design-Expert software will calculate the optimum condition.

Table 4.16 The range of variables to determine the optimum conditions of catalytic cracking of waste chicken fat over coal fly ash catalyst by using Design Expert program.

Name	Goal	Lower Limit	Upper Limit	Unit
Temperature (A)	is in range	420	460	°C
Time (B)	is in range	45	75	Minute
Catalyst (C)	is in range	1	5	%wt
Pressure (D)	is in range	1	5	Bar
Yield of gas	minimize	-	-	%wt
Yield of solid	minimize	-	-	%wt
Yield of liquid	maximize	-	-	%wt
Yield of naphtha	maximize	-	-	%wt
Yield of diesel	maximize	-	-	%wt

The optimum condition is the reaction temperature of 445 °C, the reaction time of 45 minutes; the amount of the fly ash catalyst is 1 percent by weight; and the initial hydrogen pressure of 1 bar. The highest 76.62%wt yield of liquid fuel, 19.54%wt gas, and 3.84%wt solid, respectively. At this condition, the compositions of liquid product are 21.33%wt gasoline, and 31.00%wt diesel, respectively as shown in Table 4.17.

Table 4.17 The optimum conditions of catalytic cracking of waste chicken fat over fly ash catalyst between Design-Expert program and the actual experiment.

	Optimum condition	
	Program	**Actual Experimental**
Product distribution (%wt)		
liquid	76.21	76.62
gas	18.39	19.54
solid	5.39	3.84
Oil composition (%wt)		
naphtha	23.98	21.33
Diesel	30.44	31.00

4.4.1 Comparison between thermal cracking and catalytic cracking in a batch reactor

In Table 4.18, the overall material balances obtains the thermal and catalytic cracking processes in batch reactor. The values in this table presents catalytic cracking, which provides a considerable increase of liquid yield than thermal cracking. There are significant changes in the yield of oil composition, generating a higher yield of naphtha from 17.00 %wt. to 21.33 % wt. and lower yield of long residues from 41.00 %wt. to 34.34 % wt. Thus, catalytic cracking is more efficient than thermal cracking.

Table 4.18 Mass balance and fractions of biofuel from cracking processes

	Optimum condition	
	Thermal cracking	**Catalytic cracking**
Product distribution (%wt)		
liquid	67.74	76.62
gas	28.86	19.54
solid	3.4	3.84
Oil composition (%wt)		
naphtha	17.00	21.33
Diesel	29.00	31.00
LR	41.00	34.34

4.4.2 Comparison between catalytic cracking uses coal fly ash catalyst and other metal oxide catalyst at optimum condition.

Table 4.19 indicates all compositions of product from coal fly ash catalyst in cracking process, comparing with other metal oxide catalyst. The result from coal fly ash catalyst gives percentage of liquid product and naphtha yield of 76.46 %wt and 21.33 %wt, respectively. Comparing with other catalysts (CaO, MgO, and dolomite), they are found the quantity of liquid product in rang of 79.85-80.87 %wt., whereas the percentage of liquid product from coal fly ash catalyst is 76.46 %wt. The ultimate analysis of liquid product which is the analysis of elements. It is also found that the oxygen content of CaO, MgO and dolomite as a catalyst give a lower oxygen content than using coal fly ash catalyst, the evidence proves that the use of base catalyst can decreases oxygen content due to decarboxylation and decarbonylation [33, 62]. Decreasing of oxygen content directly affects heating value. Therefore, the heating value is inversely variation with the oxygen content as shown in Table 4.19. The result shows that heating value of biofuel increase from 42.96 to 48. 35 MJ/kg. To summarize, the use of coal fly ash catalyst has a potential utilize in cracking process.

Table 4.19 Comparison the composition of biofuel with fly ash catalyst and other metal oxide catalyst

	Catalyst			
	Fly ash	**CaO**	**MgO**	**Dolomite**
Product distribution (%wt)				
Liquid	76.46	79.85	80.87	80.17
Gas	19.54	15.95	15.33	15.63
Solid	4.00	4.20	3.80	4.20
Oil composition (%wt)				
Naphtha	21.33	23.00	24.00	25.00
Diesel	31.00	34.00	33.00	34.00
LR	34.34	29.00	29.00	27.00
Ultimate analysis (%wt)				
Oxygen	12.75	11.25	11.79	10.05
Fuel Property				
Hating value (MJ/kg)	42.96	45.88	43.65	48.35

4.5 Univariate analysis for the catalytic cracking of waste chicken fat on fly ash catalyst.

4.5.1 The effect of temperature

In accordance with Fig.4.9, the effect of temperature on the product yield is activated on 415 °C - 460 °C temperature by breaking-down the chains hydrocarbon from large chain to small chain [46, 47, 52, 53]. This is because higher reaction temperature cracks continuously hydrocarbon molecules until some of naphtha are converted into hydrocarbon gas. The possible reason for these results can be that the effect of temperature in thermal degradation is significant, in the first step start with cracking by radical and removal of CO and CO_2 from triglycerides to di-glycerides and mono-glycerides. Afterward, hydrolysis reaction and further degradation of long chain hydrocarbon into non-condensate gas produce higher gas content. Whereas, at low temperature (415˚C), the fraction of liquid product, solid product, and gas product are 87.21 %wt., 3.13%wt., and 9.60 %wt. When the cracking temperature increases, the liquid yield obviously decreases form 82.67 %wt. at 430 ˚C to 60.11wt% at 470 ˚C while the gas fraction shows significant increase from 15.80 %wt. at 430 ˚C to 30.57%wt at 460 ˚C.
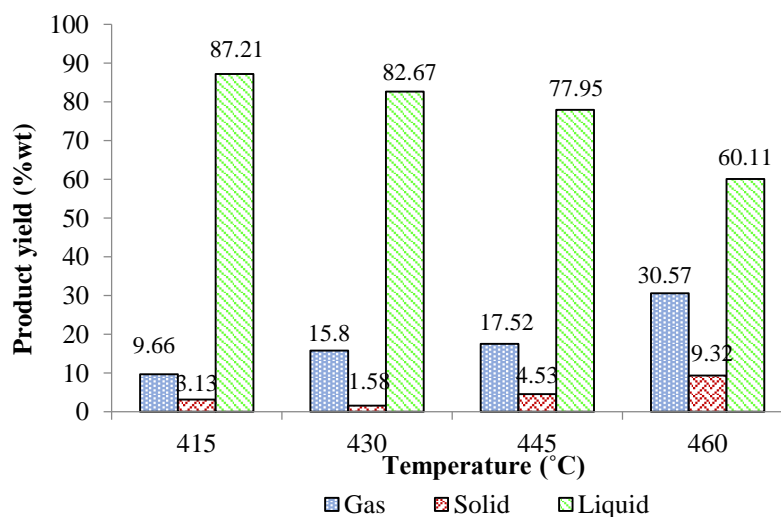
Fig. 4.9 The effect of temperature on product yield where initial hydrogen pressure of 1 bar, reaction time 45 minutes and 1%wt of coal fly ash catalyst content.

The characterization of oil fractions in liquid product uses simulated distillation gas chromatography. Liquid fuels are obtained in the range of naphtha, kerosene, diesel and long residue, respectively. The effect of temperature cracks into the naphtha yield as shown in Fig. 4.10. When the temperature is increased from 415 °C to 460 °C, thermal cracking within system can thoroughly occur. Large hydrocarbon molecules are cracked into medium hydrocarbon molecules. After that, the catalyst played a role in the selectivity to produce small hydrocarbon molecules, which result in higher percentage of naphtha yield [63, 64]. For fly ash catalyst, percentage of naphtha yield increases when reaction temperature is higher. The high contents of Si and Al in fly ash is suitable to use in the catalytic cracking process [54]. The high content of those metals can enhance the generation of hydroxyl radical and the acceleration of the catalytic process [65, 66].When increase temperature hydroxyl radical and accelerate, the catalytic process cracks the long chain of hydrocarbon molecule into a middle hydrocarbon molecule such as kerosene and diesel fraction [66]. Thereafter kerosene, diesel is catalytically cracked converting them into naphtha and gaseous.
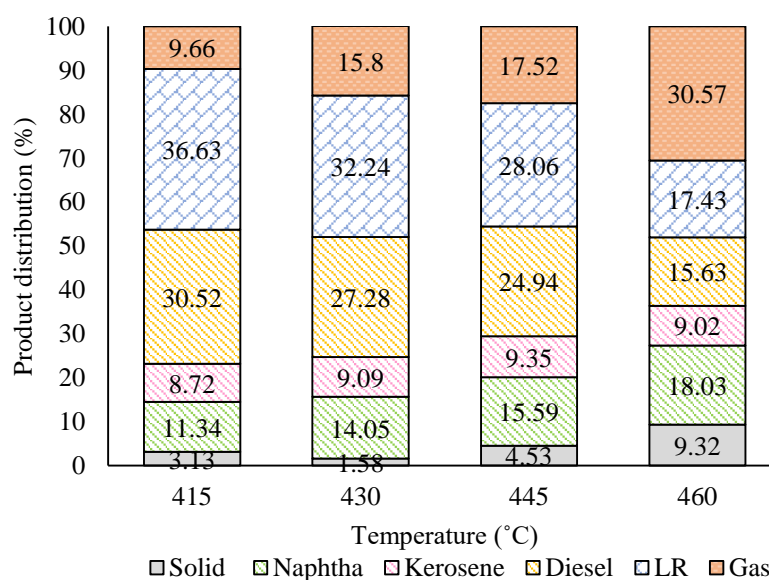
Fig. 4.10 The effect of temperature on product distribution where initial hydrogen pressure of 1 bar, reaction time 45 minutes and 1%wt of coal fly ash catalyst content.

4.5.2 The effect of reaction time

Fig. 4.11 is shown the product yield when reaction time is increased from 45 min to 75 min. Waste chicken fat is continuously cracked along the reaction time [[21, 47]. The percentage of liquid product is lower as shown in Fig 4.11. The yields of liquid product decrease from 77.95 %wt. at 45 min to 71.00 %wt. at 75 min. In addition, the gases content and the yield of solid are slightly increased. Long contact time in batch reactor leads to lower liquid fuel. These reactions consequently increase the cracking process of long chain hydrocarbon to short chain hydrocarbon. As the result, gas product is increased.
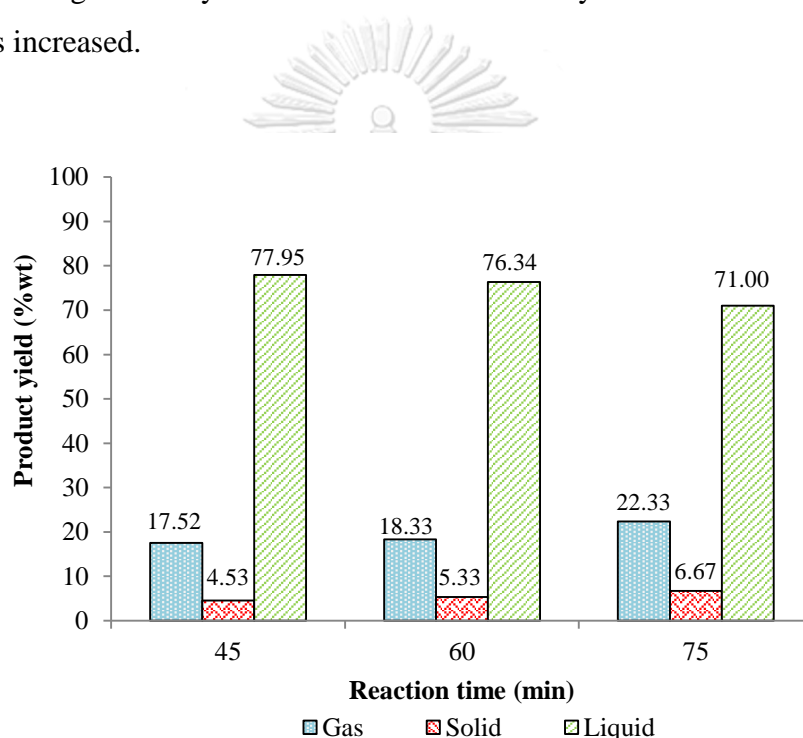
Fig. 4.11 The effect of reaction time on liquid product where reaction temperature of 445 °C, initial hydrogen pressure of 1 bar and 1%wt of coal fly ash catalyst content.

Fig. 4.12 is shown the effect of reaction time on the product distribution. When reaction time is increased from 45 to 75 min., large hydrocarbon molecules are continuously converted to smaller hydrocarbon molecules. The result of increase reaction time shows that the gaseous products increase, whereas, the product distribution such as naphtha decreased, kerosene and diesel are slightly changed. The longer reaction time the cracking can be better proceeded. When the reaction time is further continued, some of naphtha is converted into gases. Gaseous product increases

from 17.52 %wt. at 45 min to 22.33 %wt. at 75 min. The increased temperature and reaction time give the higher yield of gas product.
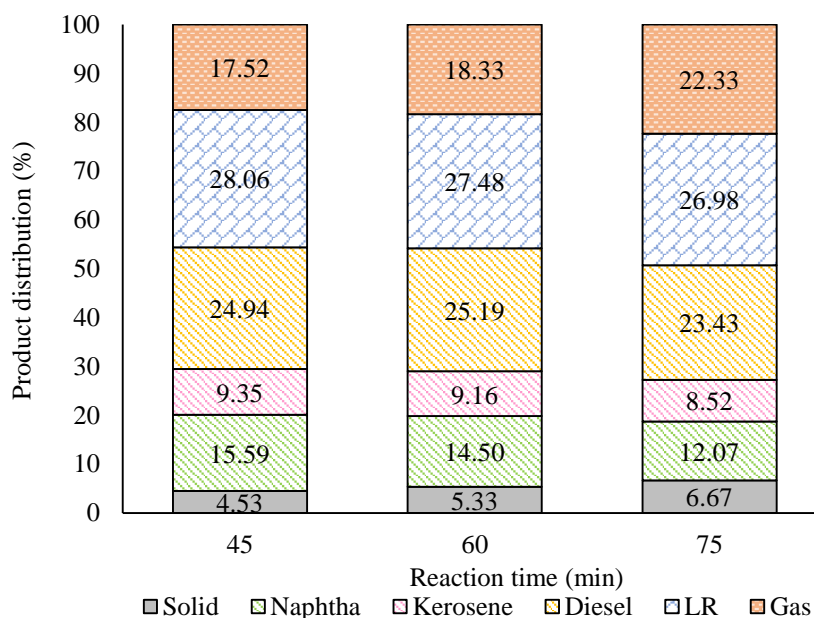
Fig. 4.12 The effect of reaction time on product distribution where reaction temperature of 445 ˚C, reaction , initial hydrogen pressure 1 bar and 1%wt of coal fly ash catalyst content.

4.5.3 The effect of the catalyst content

From Fig.4.13, it observes that when increasing catalyst content from 1.0 %wt. to 5.0 %wt., percentage of liquid product and gaseous product are steady changed. The liquid yield is gradually deceased from 77.89 %wt. to 75.03 %wt. Moreover, the result of 7 percentages of catalyst increase gas yield up to 26.67 %wt., which is the highest produce when compare to less than 7 percentages. It can be concluded that with more catalyst content, the cracking reactivity makes an amount of gas product. The cleavage of C-C carboniumion bonds in α and β positions while decarboxylation, decarbonylation, dehydratio produce a smaller hydrocarbon. After that, the role of catalyst also occur hydrogen transfer, hydrogenation, Dehydrogenation and isomerization reaction to produce olefins and paraffins.
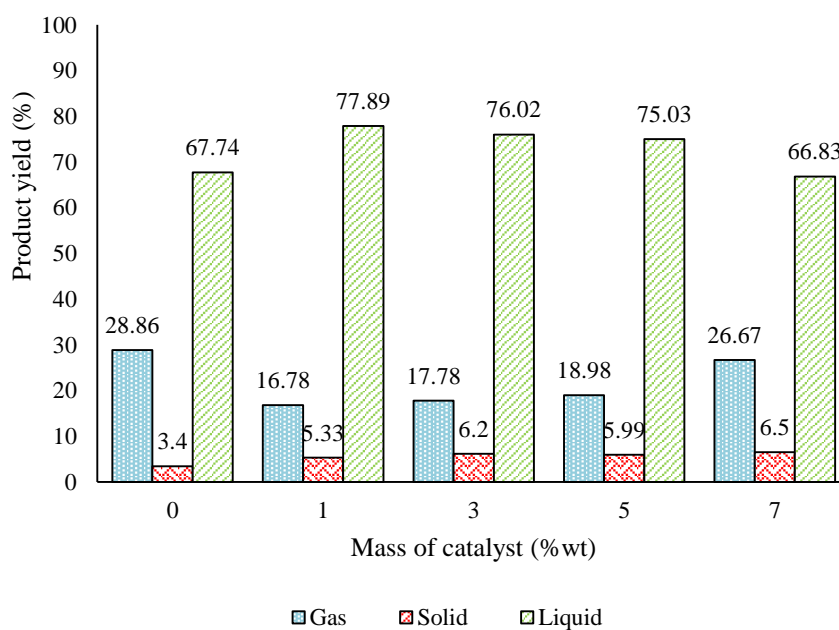
Fig. 4.13 The effect of the catalyst content on product yield, reaction temperature of 445 °C, reaction time of 45 minutes and initial hydrogen pressure of 1 bar.

Considering percentage of product distribution as shown in Fig. 4.14, it is found that all catalysts result in lower percentage of diesel yield. The more catalyst content can rise cracking process conduce long residue into lighter oil such as kerosene and naphtha. It can be concluded that when catalyst content increase percentage of naphtha yield and long residues decrease, while gashouse product is risen.
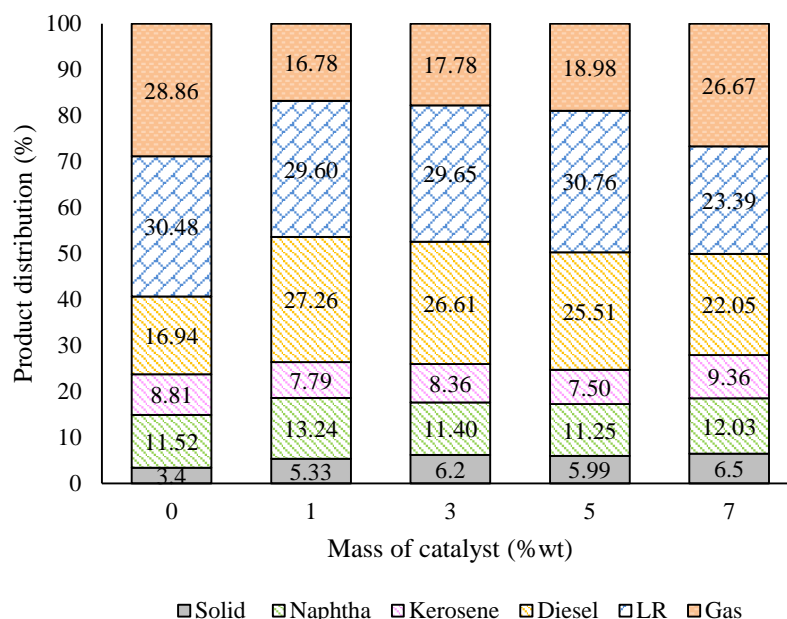
Fig. 4.14 The effect of catalyst content on product distribution, reaction temperature of 445 °C, reaction time of 45 minutes and initial hydrogen pressure 1 bar.

4.5.4 The effect of initial hydrogen pressure

The effect of initial hydrogen pressure on the product yield is shown in Fig.4.15. It is found that increasing initial hydrogen pressure from 1 bar to 5 bar do not significantly influence on percentage of liquid product. Increasing initial hydrogen pressure do not influence on the percentage of liquid product comparing with the effects of temperature and reaction time. The percentage of liquid product is slightly decreased. No-used H_2 pressure, the data reveals that a lower percentage of liquid product (62.41%wt). Moreover, it is presented higher percentage of gaseous product. It concludes that the effect of initial hydrogen pressure is significant for the catalytic cracking because hydrogen pressure provides hydrogenation and hydrocracking reaction in the cracking process. In addition, hydrogen pressure promotes rearrangement of smaller hydrocarbon molecule. Whereas unfilled H_2 pressure can increase thermal cracking of large hydrocarbon molecules into small hydrocarbon molecules. Therefore, the opportunities that small hydrocarbon molecules would crack into gases are higher. Furthermore, hydrogen pressure favors the hydrogenate reaction,

further decomposition of C-C bonds. The one of advantages of hydrogen pressure in reaction is hydrogenation of alkenes over polymerization and condensation without any substantial coke on the surface of catalyst.
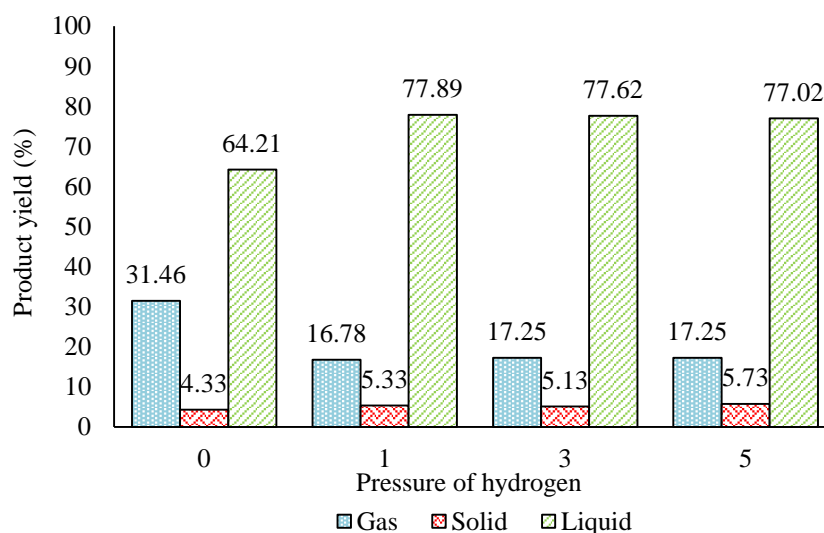
Fig. 4.15 The effect of initial hydrogen pressure on product yield, reaction temperature of 445 °C, reaction time of 45 minutes and 1%wt of coal fly ash catalyst content.

Fig. 4.16 is shown product distribution of liquid product which is observed that when increase initial hydrogen pressure from 0 bar to 5 bar. It is found the effect of initial hydrogen pressure from 1– 5 bars is insignificant when increasing pressure, percentage of naphtha yield slightly decreased. It is possible that H_2 enhances cracking hydrocarbon molecules. Comparison with unfilled H_2 pressure, the data shows that a small hydrocarbon molecules can be cracked better. Some of naphtha further crack into more gases as shown in Fig.4.16.
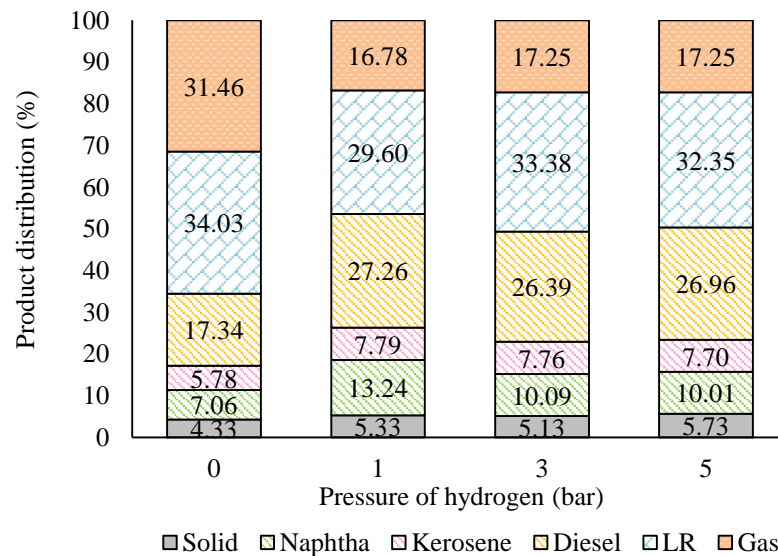
Fig. 4.16 The effect of initial hydrogen pressure on product distribution, reaction temperature of 445 °C, reaction time of 60 minutes and 1%wt of catalyst content.

4.6 Kinetic Study [67, 68]

Cracking mechanism is the mostly complex reaction. The assumption of mechanism of catalytic cracking of waste chicken fat to liquid fuels is investigated by kinetics study. The boundary condition in Fig. 4.17as follows:

Conversion at the initial time: X_{B0}

Conversion at the time: X_B

Initial concentration of reactant: C_{B0}

Initial concentration of reactant at time: C_B

Fig. 4.17 The boundary of kinetic study.

The kinetics variables are temperature of 410, 430, 450 and 470 °C, and reaction time 0-75 minutes under initial hydrogen pressure of 1 bar with 1 %wt. of coal fly ash catalyst. The variables condition of kinetic study is shown in Table 4.20.

Table 4.20 The kinetic condition of catalytic cracking.

| Catalyst | Kinetics Study | | | |
	Temperature (°C)	Reaction time (min)	Initial hydrogen pressure (bar)	Catalyst Content (%wt)
Fly ash	410, 430, 450, 470	0,5,10,15,20,25,30, 35,40,45,50,55,60,65 70,75	1	1

The cracking mechanism is occurred in batch reactor. This kinetics study investigates long residue in waste chicken fat under reaction time. The assumption of kinetic model as following details: the reaction is isothermal at the setting temperature for each batch of reaction under the initial pressure of hydrogen and constant of liquid volume as indicated in Table 4.20. The conversion of long residue (LR) for each desire temperature can be calculated from the analysis of long residue, where the conversion at initial time is X_{B0} and at the time, t is X_B.

$$\% \text{ Conversion of long residue} = \left(\frac{X_{B0} - X_B}{X_{B0}}\right) \times 100 \qquad (4.4)$$

Thus, the black part of the reactor (from Fig. 4.17) can be represented by the equation rate of disappearance of B = the rate of the conversion of B per volume

$$-r_B = \left(-\frac{1}{V}\right)\left(\frac{dn_B}{dt}\right) \qquad (4.5)$$

It was assumed that N_{B0} is the beginning amount of LR in the reactor at time = 0 and N_B is the LR amount at time t. Then, the conversion of LR is defined.

$$X_B = \left(\frac{N_{B0} - N_B}{N_B}\right) = 1 - \frac{N_B/V}{N_{B0}/V} \qquad (4.6)$$

$$X_B \quad = \quad 1 - \frac{C_B}{C_{B0}} \tag{4.7}$$

C_B is the LR concentration at the time (min) and C_{Bo} is the initial concentration

As the reaction occurred in constant volume reactor, the concentration is written in the form as in equation

$$-r_B \quad = \quad (-dc_b/dt) \quad = k_n C_B^n \tag{4.8}$$

If first order reaction is obtain the relationship between $-r_B$ and C_B from the equation 4.8 as follow

$$(-dc_B/dt) \quad = \quad k_1 C_B \tag{4.9}$$

$$-\int_{C_{B0}}^{C_B} dC_B / C_B \quad = \quad k_2 \int_0^t k_1 dt \tag{4.10}$$

Integrating

$$\ln(C_B) - \ln(C_{B0}) = \quad -k_1 t \tag{4.11}$$

Thus

$$\ln(C_B) = \quad \ln(C_{B0}) - k_1 t \tag{4.12}$$

A plotted of ln (C_B) versus t gives the straight line with slope $= -k_1$

If second order reaction is obtain the relationship between $-r_B$ and C_B from the equation 4.8 as follow

$$(-dc_B/dt) \quad = \quad k_2 C_B^2 \tag{4.13}$$

$$-\int_{C_{B0}}^{C_B} dC_B / C_B^2 \quad = \quad k_2 \int_0^{t_B} dt \tag{4.14}$$

Integrating

$$(1/C_B) - (1/C_{B0}) \quad = \quad k_2 t \tag{4.15}$$

$$(1/C_B) \quad = \quad (1/C_{B0}) + k_2 t \tag{4.16}$$

A plotted of $(1/C_B)$ versus t gives the straight line with slope $= k_2$

4.6.1 The kinetic study of catalytic cracking waste chicken fat on fly ash catalyst

    The experiment is creaked in batch reactor. The reaction is finished by stop heating and cooling the reactor through a cold water. The conversion of long residue at the difference of reaction time is shown in table 4.21

Table 4.21 The conversion of long residue at the difference of reaction time of catalytic cracking waste chicken fat over coal fly ash catalyst.

Temperature (˚C)	Time (min)	LR (%wt)	Conversion	ln(1-X)	X/(1-X)
410	0	60.00	0.0000	0.0000	0.0000
	5	60.00	0.0000	0.0000	0.0000
	10	59.50	0.0083	-0.0084	0.0085
	15	58.00	0.0333	-0.0339	0.0345
	20	57.00	0.0500	-0.0513	0.0526
	25	55.50	0.0750	-0.0780	0.0812
	30	55.50	0.0750	-0.0780	0.0812
	35	54.50	0.0917	-0.0962	0.1010
	40	54.00	0.1000	-0.1055	0.1115
	45	53.50	0.1083	-0.1147	0.1216
	50	53.00	0.1167	-0.1241	0.1321
	55	53.00	0.1167	-0.1241	0.1321
	60	52.00	0.1333	-0.1431	0.1538
	65	52.00	0.1333	-0.1431	0.1538
	70	51.00	0.1500	-0.1627	0.1769
	75	49.50	0.1750	-0.1924	0.2122
430	0	50.00	0.0000	0.0000	0.0000
	5	50.00	0.0000	0.0000	0.0000
	10	48.50	0.0300	-0.0305	0.0310
	15	46.50	0.0700	-0.0726	0.0754
	20	43.50	0.1300	-0.1393	0.1496
	25	42.00	0.1600	-0.1746	0.1912
	30	41.50	0.1700	-0.1864	0.2050
	35	39.50	0.2100	-0.2358	0.2660
	40	39.00	0.2200	-0.2485	0.2821
	45	38.50	0.2300	-0.2614	0.2989
	50	38.00	0.2400	-0.2744	0.3158
	55	37.50	0.2500	-0.2878	0.3336
	60	37.00	0.2600	-0.3011	0.3514

	65	37.00	0.2600	-0.3011	0.3514
	70	36.50	0.2700	-0.3148	0.3701
	75	36.00	0.2800	-0.3285	0.3889
450	0	41.00	0.0000	0.0000	0.0000
	5	37.50	0.0854	-0.0893	0.0935
	10	37.00	0.0976	-0.1027	0.1081
	15	35.50	0.1341	-0.1441	0.1552
	20	35.00	0.1463	-0.1582	0.1714
	25	34.00	0.1707	-0.1872	0.2059
	30	33.50	0.1829	-0.2021	0.2242
	35	33.00	0.1951	-0.2175	0.2436
	40	32.00	0.2195	-0.2483	0.2825
	45	31.50	0.2317	-0.2637	0.3019
	50	31.00	0.2439	-0.2796	0.3226
	55	30.50	0.2561	-0.2960	0.3446
	60	29.50	0.2805	-0.3293	0.3902
	65	28.50	0.3049	-0.3638	0.4390
	70	27.50	0.3293	-0.3996	0.4914
	75	26.00	0.3659	-0.4555	0.5769
470	0	38.00	0.0000	0.0000	0.0000
	5	33.50	0.1184	-0.1262	0.1346
	10	32.00	0.1579	-0.1723	0.1887
	15	31.00	0.1842	-0.2036	0.2258
	20	30.50	0.1974	-0.2200	0.2462
	25	29.50	0.2237	-0.2533	0.2885
	30	29.00	0.2368	-0.2703	0.3103
	35	28.50	0.2500	-0.2878	0.3337
	40	28.00	0.2632	-0.3054	0.3571
	45	27.50	0.2763	-0.3236	0.3823
	50	27.00	0.2895	-0.3417	0.4074
	55	26.00	0.3158	-0.3795	0.4615
	60	25.50	0.3289	-0.3991	0.4908
	65	24.50	0.3553	-0.4391	0.5517
	70	23.50	0.3816	-0.4808	0.6178
	75	23.00	0.3947	-0.5021	0.6522

From Table 4.21, column ln (1-x) and x/(1-x) are for first and second reaction order, respectively. When ln (1-x) [equation 4.11] and time are plotted as graph. The first reaction shows the negative axis in Fig.4.18. When x(1-x) [equation 4.16] and

time are plotted, the second reaction shows the positive axis in Fig.4.19. The conversion of long residues to liquid product over coal fly ash catalyst is validated at temperature 410, 430, 450 and 470°C, and reaction time at 0-75 minutes. It give precisely a right line with a good regression constant nearby 1.00.
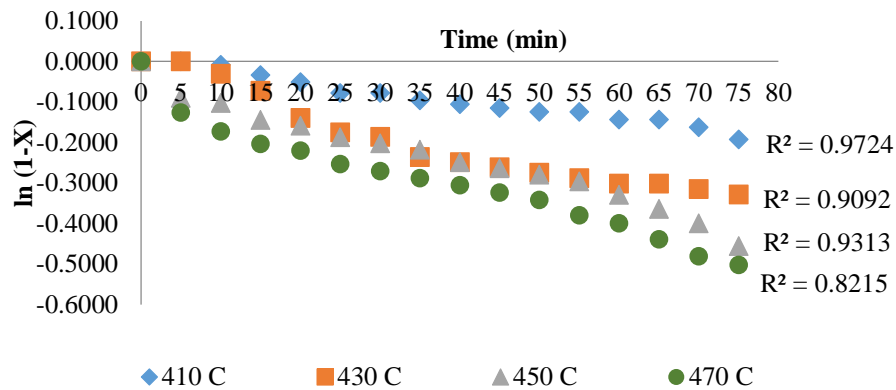
Fig. 4.18 Conversion vs. time of reaction for first order.
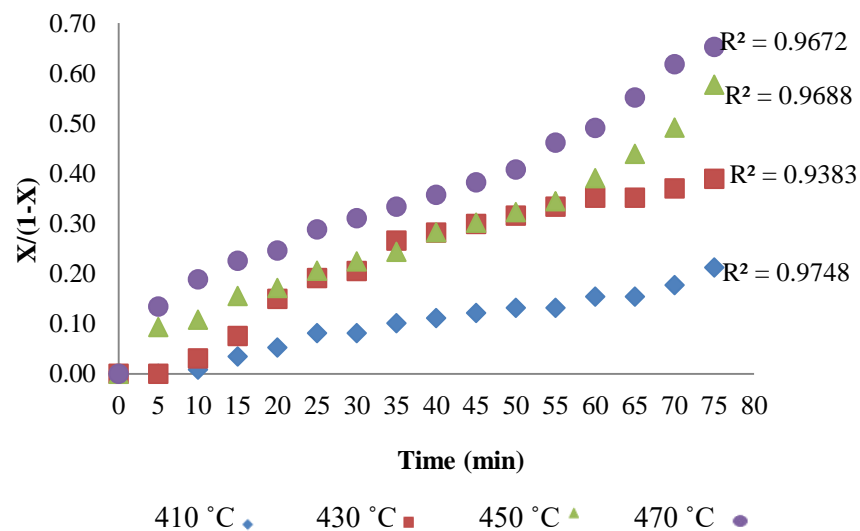
Fig. 4.19 Conversion vs. time of reaction for second order.

The experiment data in Fig 4.18 and 4.19 will be used to find the estimate R^2 near 1.00. In conclude, the second order nearer 1.00 than first order.

The equation 4.8 for second order become

$$(1/C_B) - (1/C_{B0}) = k_2 t \qquad (4.17)$$

$$(1/C_B) = (1/C_{B0}) + k_2 t \qquad (4.18)$$

Rearrange in term of conversion

$$X = 1 - (C_B/C_{B0}) \qquad (4.19)$$

Therefore

$$K_2 C_{Bo} t = (1/(1-X)) - 1 \qquad (4.20)$$

Consideration the rate constant at the various temperature and plot the relationship between $\ln(k_2)$ and $1/T$ from Arrhenius's equation

$$k_n = k_{(n0)} e^{(-E/RT)} \qquad (4.21)$$

The equation is expression in term of logarithm as following

$$\ln(k_n) = \ln(k_{n0}) - (E/R)/T \qquad (4.22)$$

A plot of $\ln(k_n)$ versus $1/T$ gives the straight line with the slope as $(-E/R)$ and the intercept $= \ln(k_{n0})$ which uses to determine the activation energy (Ea) and Pre-exponential (k_{n0}), respectively.

Table 4.22 Values of $\ln(k_n)$ versus $1/T$ at the variation of reaction temperature.

Temperature (°C)	$1/T$ (K^{-1})	$k_2 C_{B0}$ (min^{-1})	$k_2 C_{B0}$ (s^{-1})	$\ln(k_2)$
410	1.4641×10^{-3}	0.0026	4.50×10^{-5}	-10.0088
430	1.422×10^{-3}	0.0050	8.33×10^{-5}	-9.3926
450	1.3383×10^{-3}	0.0064	1.07×10^{-4}	-9.1458
470	1.345×10^{-3}	0.0097	1.62×10^{-4}	-8.7299

Fig. 4.20 Plot of values of logarithmic specific reaction rate constant against the reciprocal of the reaction temperature.

Fig. 4.20 demonstrates ln k versus 1/T. E_a (activation energy) can be obtained by the slope of the straight line. It can calculate k_0 (Pre-exponential or frequency factor) from intercept.

Therefore,

$$E_a = 85.97 \text{ kJ mol}^{-1} \quad ; \quad k_0 = 1.01 \times 10^3 \text{ s}^{-1}$$

4.6.2 The kinetic study of thermal cracking waste chicken fat on fly ash catalyst

The experiments are conduct at temperature of 410, 430, 450 , 470°C without coal fly ash catalyst.

Table 4.23 The conversion of long residue at the difference of reaction time cracks waste chicken fat over fly ash catalyst.

Temperature (˚C)	Time (min)	LR (%wt)	Conversion	ln(1-X)	X/(1-X)
410	0	56.00	0.0000	0.0000	0.0000
	5	55.00	0.0179	-0.0180	0.0182
	10	54.00	0.0357	-0.0364	0.0370
	15	52.00	0.0714	-0.0741	0.0769
	20	52.00	0.0714	-0.0741	0.0769
	25	52.00	0.0714	-0.0741	0.0769
	30	51.00	0.0893	-0.0935	0.0980
	35	50.00	0.1071	-0.1133	0.1200
	40	48.00	0.1429	-0.1542	0.1667
	45	45.00	0.1964	-0.2187	0.2444

	55	42.00	0.2500	-0.2877	0.3333
	60	41.00	0.2679	-0.3118	0.3659
	65	40.00	0.2857	-0.3365	0.4000
	70	40.00	0.2857	-0.3365	0.4000
	75	39.00	0.3036	-0.3618	0.4359
430	0	54.00	0.0000	0.0000	0.0000
	5	53.00	0.0185	-0.0187	0.0189
	10	51.00	0.0556	-0.0572	0.0588
	15	48.00	0.1111	-0.1178	0.1250
	20	45.00	0.1667	-0.1823	0.2000
	25	44.00	0.1852	-0.2048	0.2273
	30	41.00	0.2407	-0.2754	0.3171
	35	39.00	0.2778	-0.3254	0.3846
	40	38.00	0.2963	-0.3514	0.4211
	45	36.00	0.3333	-0.4055	0.5000
	50	35.00	0.3519	-0.4336	0.5429
	55	34.00	0.3704	-0.4626	0.5882
	60	34.00	0.3704	-0.4626	0.5882
	65	33.00	0.3889	-0.4925	0.6364
	70	33.00	0.3889	-0.4925	0.6364
	75	33.00	0.3889	-0.4925	0.6364
450	0	33.00	0.0000	0.0000	0.0000
	5	33.00	0.0000	0.0000	0.0000
	10	32.00	0.0303	-0.0308	0.0313
	15	31.00	0.0606	-0.0625	0.0645
	20	30.00	0.0909	-0.0953	0.1000
	25	29.00	0.1212	-0.1292	0.1379
	30	28.00	0.1515	-0.1643	0.1786
	35	27.00	0.1818	-0.2007	0.2222
	40	26.00	0.2121	-0.2384	0.2692
	45	25.00	0.2424	-0.2776	0.3200
	50	24.00	0.2727	-0.3185	0.3750
	55	23.00	0.3030	-0.3610	0.4348
	60	22.00	0.3333	-0.4055	0.5000
	65	21.00	0.3636	-0.4520	0.5714
	70	21.00	0.3636	-0.4520	0.5714
	75	21.00	0.3636	-0.4520	0.5714
470	0	34.00	0.0000	0.0000	0.0000
	5	27.00	0.2059	-0.2305	0.2593
	10	26.00	0.2353	-0.2683	0.3077
	15	25.00	0.2647	-0.3075	0.3600
	20	24.00	0.2941	-0.3483	0.4167
	25	23.00	0.3235	-0.3909	0.4783
	30	22.00	0.3529	-0.4353	0.5455
	35	22.00	0.3529	-0.4353	0.5455
	40	21.00	0.3824	-0.4818	0.6190
	45	21.00	0.3824	-0.4818	0.6190

50	20.00	0.4118	-0.5306	0.7000
55	20.00	0.4118	-0.5306	0.7000
60	19.00	0.4412	-0.5819	0.7895
65	18.00	0.4706	-0.6360	0.8889
70	18.00	0.4706	-0.6360	0.8889
75	17.00	0.5000	-0.6931	1.0000

Table 4.23 presents the data for plotting of second reaction order in thermal cracking process. Graph of x(1-x) [equation 4.13] and time found that the second reaction order crossed the positive axis as shown in Fig.4.21.
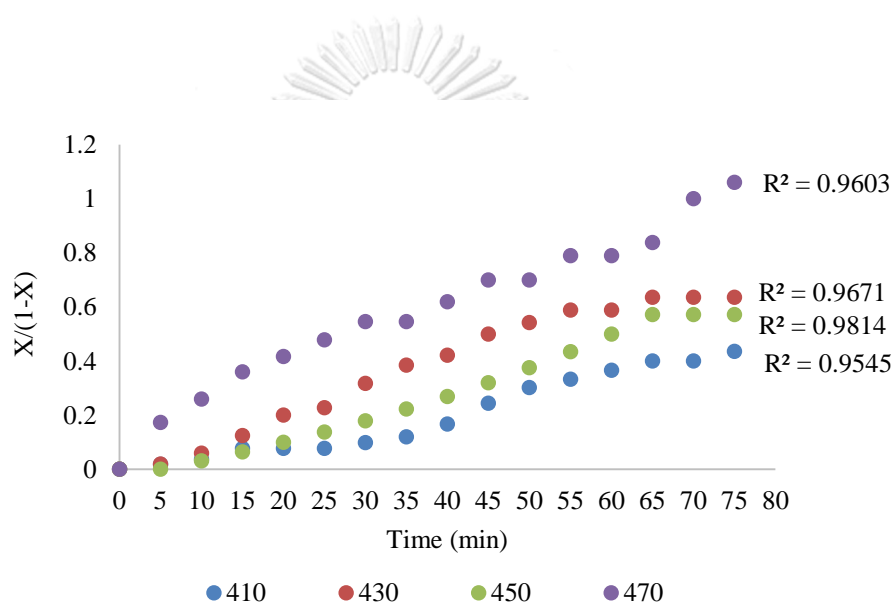
Fig. 4.21 Conversion vs. time of reaction for second order.

Table 4.24 Established of ln(k_n) versus 1/T at the variation of reaction temperature.

Temperature (°C)	1/T (K^{-1})	$k_2 C_{B0}$ (min^{-1})	$k_2 C_{B0}$ (s^{-1})	ln(k_2)
410	1.4641 x 10^{-3}	0.0019	3.17 x 10^{-5}	-10.3602
430	1.422 x 10^{-3}	0.0036	6.00 x 10^{-5}	-9.72117
450	1.3383 x 10^{-3}	0.0072	1.20 x 10^{-4}	-9.02802
470	1.345 x 10^{-3}	0.0091	1.52 x 10^{-4}	-8.79383

Fig. 4.22 Plot of values of logarithmic specific reaction rate constant
beside the reciprocal of the reaction temperature.

Fig. 4.22 shows ln k versus 1/T. Ea, the activation energy can be obtained from the slope of the straight line and $\ln(k_0)$ as an intercept. The calculation of kinetics parameter is determined by the Arrhenius equation as shown in equation 4.22.

Therefore

$$Ea = 120.86 \text{ kJ mol}^{-1} \quad ; \quad k_0 = 5.41 \times 10^4 \text{ s}^{-1}$$

Thermal cracking of waste chicken fat given activation energy is 120.86 kJ mol^{-1}, whereas, the catalytic cracking can reduce activation energy to 85.97 kJ mol^{-1}. Catalyst can provide a lower activation energy of reaction. The order of reaction present in second order because the long residues decompose to diglycerides, monoglycerides, carboxylic acid, ketones and aldehydes. The next reaction removes oxygen of heavy oxygenated with decarboxylation, decarbonylation and dehydration. After that, thermal cracking (radical scission) and catalytic cracking (β- scission) can crack long chain hydrocarbon into smaller chain hydrocarbon.

4.6.3 Comparison of kinetics study with other literature

The comparing kinetics study in this research with other literature as shown in Table 4.25, the data will be compared kinetics parameters, which are activation energy and order of reaction.

In this work, the experiments carried out under the isothermal conditions in a batch reactor. The average values obtain for two duplicate with a reaction time varying from $0 - 75$ min. The second order mechanism is the order reaction for cracking waste chicken fat on the coal fly ash catalyst and activation energy is 85.97 kJmol^{-1}, respectively, which is similar to a kinetic study of Samia A. Hanaf et al. [57]. They investigated kinetic study of waste chicken fat using NiW/SiO$_2$–Al$_2$O$_3$, the results show that second order in their experiment. An activation energy was 96 kJmol^{-1} close to in this research. Furthermore, the other researcher examines kinetics studied of non-edible oil with consists of a large fatty acids, such as Jatropha oil and used palm oil as a feedstock. The evidence indicated that activation energy from cracking of non-edible oil was 127 and 118.00 kJ mol^{-1}, respectively [16, 69]. The activation energy from waste animal fat and non-edible oil show the value of 96-127 kJ mol^{-1}, it indicates the activation energy in other literature close to in this work.

The possible pathway of the catalytic cracking process as illustrated in Fig 4.23. [47, 65, 70-73]. The waste chicken fat consists of mainly triglyceride, accordingly there are several possible reaction pathways for production of small-chain hydrocarbons. Fatty acids can be directly removed oxygen content by deoxygenation. The direct decarboxylation removes the carboxyl group by releasing carbon dioxide and producing a paraffin hydrocarbon, while direct decarbonylation produces an olefin hydrocarbon and the product of the carboxyl group by forming carbon monoxide and water. Additionally, the fatty acid can be deoxygenated by adding hydrogen, in this pathway, the production of linear hydrocarbon can follow by hydrogenation. The C-C bond cleavage reaction by thermal and catalytic cracking. The radical scission from thermal cracking favor a high yield of smaller hydrocarbon components, with a coke production. The catalytic cracking occur via carbonium ion at α and β-scission at the acidic sites of the catalyst. The olefins obtained by dehydrogenation of saturates on the metallic sites and hydrocarbon rearrangement may take place, or the carbonium ion cracks into smaller hydrocarbon which hydrogenation reaction.

Table 4.25 The comparison of kinetics study of other literature

	This work	Kinetics study of other literature		
		Samia A. Hanaf et al.,[57]	Mohit Anand and Anil K. Sinha [69]	Yean-Sang Ooi et al., [16]
Raw material	Waste chicken fat	Waste chicken fat	Jatropha oil	Used Palm Oil
Catalyst	Fly ash	NiW/SiO$_2$–Al$_2$O$_3$	Co–Mo/Al$_2$O$_3$	HZSM-5
Activation enegy (kJ mol^{-1})	85.97	96.00	127.00	118.00
Order of reaction	2	2	-	-
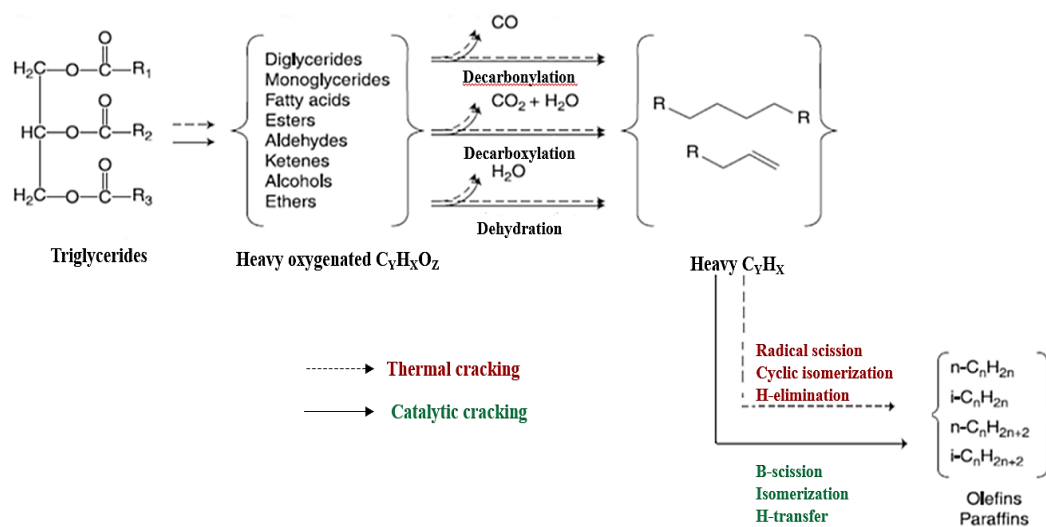
Fig. 4.23 Possible reaction pathway [73]

4.7 The study of variables that effects the catalytic cracking of waste chicken fat on fly ash in continuous reactor

The scale-up processes from 70 ml in batch reactor to 3 L in continuous reactor for the catalytic cracking of waste chicken fat on the coal fly ash catalyst is studied. Four factors in a continuous reactor and optimum condition are investigated in a 2^k experimental design. The four parameters include temperature of 420 - 460°C, feeding rate waste chicken fat of 3-9 ml/min, N_2 gas flow rate of 50-150 ml/min and catalyst content of 30-60 %V/V.

4.7.1 Percentage of liquid product

2-level factorial experimental design to determine variance of the variables affecting on percentage of liquid product in a continuous reactor as shown in Table 4.26.

It is found that percentage of liquid product in the range of 44.70-83.38 %wt., the main variables are likely to deviate from linear relationship are temperature (A), feeding rate (B), N_2 gas flow rate (C), catalyst content (D), interaction between reaction temperature and feeding rate (AB), interaction between feeding rate and catalyst content (BD) as shown in Fig. 4.24. The analysis of variance (ANOVA) is selected the confidence interval of 95 percentages. The significant variables with the P-value less than 0.05 as shown in table 4.27.

Table 4.26 Percentage of liquid product of catalytic pyrolysis of waste chicken fat over the coal fly ash catalyst in continuous reactor.

	Factor				%yield		Factor Level	
					of		Low (-)	High
Run	A	B	C	D	Liquid			(+)
1	420	3	50	30	58.76	A (ºC)	420	460
2	460	3	50	30	71.93	B (ml/min)	3	9
3	420	9	50	30	78.04	C (ml/min)	50	150
4	460	9	50	30	83.36	D (V/V)	30	60
5	420	3	150	30	55.62			
6	460	3	150	30	70.65			

7	420	9	150	30	70.91
8	460	9	150	30	74.57
9	420	3	150	60	54.65
10	460	3	50	60	67.24
11	420	9	50	60	61.94
12	460	9	50	60	69.38
13	420	3	150	60	44.70
14	460	3	150	60	63.04
15	420	9	150	60	55.35
16	460	9	150	60	64.18
17	440	6	100	45	56.82

Fig. 4.24 Half normal probability plot of percentage of liquid product from catalytic cracking of waste chicken fat on fly ash in continuous reactor.

Table 4.27 ANOVA of variables affecting on percentage of liquid product from catalytic cracking of waste chicken fat on coal fly ash in continuous reactor.

Source	Sum of Squares	df	Mean Square	F Value	p-value	
Model	1452.77	6	242.13	58.00	< 0.0001	significant
A-Temp	445.17	1	445.17	106.63	< 0.0001	
B-Feed rate	316.27	1	316.27	75.76	< 0.0001	
C-Feed rate N_2	133.83	1	133.83	32.06	< 0.0001	
D-Catalyst	434.25	1	434.25	104.02	< 0.0001	
AB	71.79	1	71.79	17.20	0.0011	
BD	51.46	1	51.46	12.33	0.0038	
Curvature	271.92	1	271.92	65.13	< 0.0001	
Residual	54.27	13	4.17			
Cor Total	1778.96	20				

The normal plot of residuals from catalytic cracking of waste chicken fat on the coal fly ash in a continuous reactor as shown in Fig. 4.25. The Normal Plot of Residuals determines the data reliable, it is found that Residuals of percentage of liquid yield tend to be straight. Adjusted R^2 and predicted R^2 show 0.9640 and 0.9474 respectively, nearby 1. The optimum percentage of liquid yield is shown in equation 4.29.
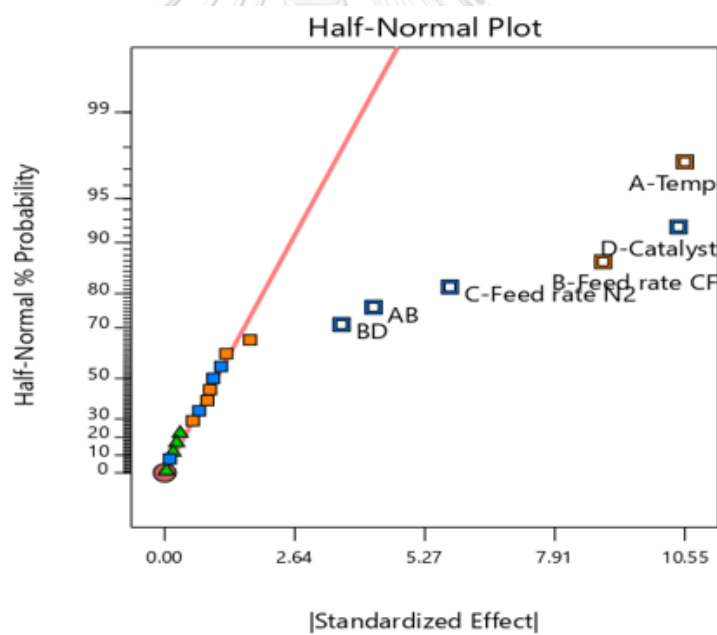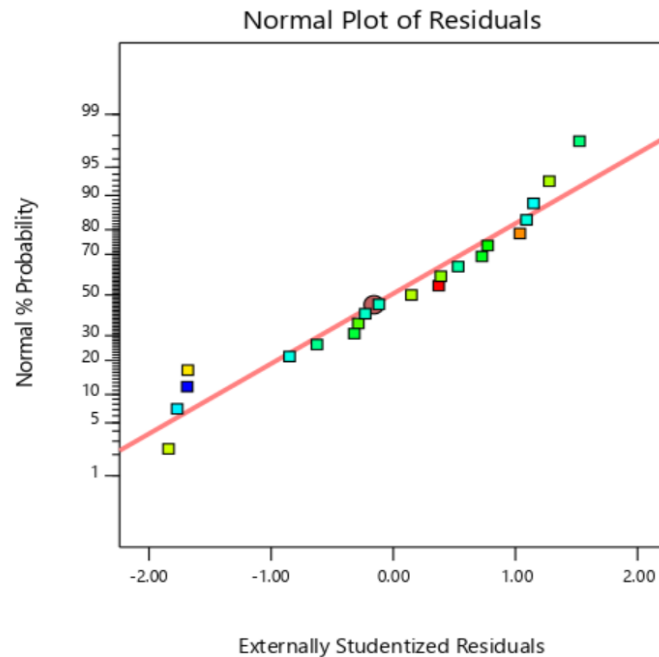
Fig. 4.25 Normal plot of residuals of percentage of liquid product from catalytic cracking of waste chicken fat on coal fly ash in continuous reactor.

$$\text{Percentage of liquid yield} = 142.21416 + 0.47556 \times A + 18.80880 \times B$$
$$-0.057843 \times C - 0.10819 \times D - 0.035303 \times A \times B$$
$$-0.039854 \times B \times D \quad\quad\quad (4.29)$$

4.7.2 Percentage of naphtha in liquid product

Table 4.28 indicates the percentage of naphtha in liquid product, it found a range of 8.75-24.82 %wt. In Table 4.29, ANOVA analysis of variables affects to the percentage of naphtha in liquid product, it is observed that the main variables A, B, D, AB, BD where the temperature (A), feeding rate (B) and catalyst content (D). Half normal probability plot of the percentage of naphtha in liquid product as shown in Fig 4.26

Table 4.28 Percentage of naphtha in liquid product from catalytic cracking of waste chicken fat on coal fly ash in continuous reactor.

Run	Factor A	B	C	D	%yield of Naphtha		Factor Level Low (-)	High (+)
1	420	3	50	30	11.56	A (°C)	420	460
2	460	3	50	30	15.00	B (ml/min)	3	9
3	420	9	50	30	10.81	C (ml/min)	50	150
4	460	9	50	30	13.88	D (V/V)	30	60
5	420	3	150	30	8.75			
6	460	3	150	30	13.75			
7	420	9	150	30	9.56			
8	460	9	150	30	19.06			
9	420	3	150	60	16.88			
10	460	3	50	60	17.19			
11	420	9	50	60	13.50			
12	460	9	50	60	24.06			
13	420	3	150	60	14.38			
14	460	3	150	60	17.38			
15	420	9	150	60	18.44			
16	460	9	150	60	24.82			
17	440	6	100	45	17.03			

Table 4.29 ANOVA of variables affecting on percentage of naphtha in liquid product from catalytic cracking of waste chicken fat on coal fly ash in continuous reactor.

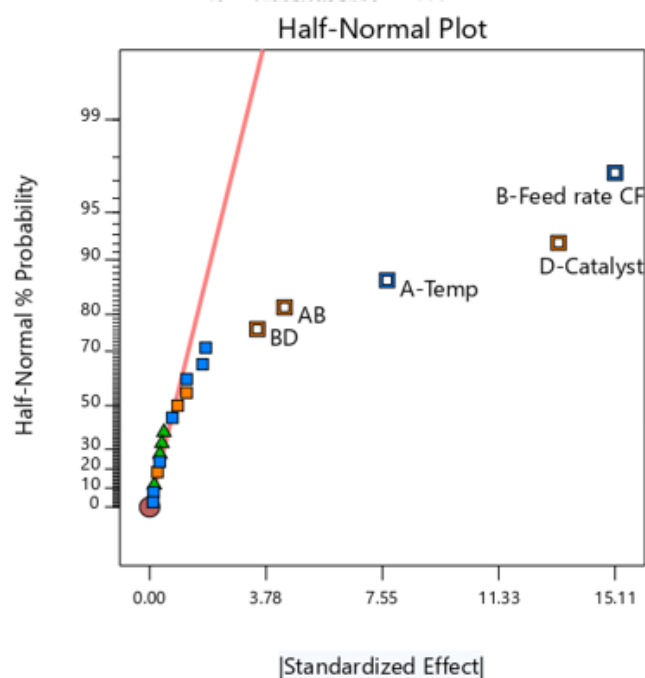| Source	Sum of Squares	df	Mean Square	F Value	p-value	
Model	550.39	6	91.73	418.55	< 0.0001	significant
A-Temp	106.35	1	106.35	28.39	0.0001	
B-Feed rate CF	23.16	1	23.16	6.18	0.0261	
D-Catalyst	122.43	1	122.43	32.69	< 0.0001	
AB	19.69	1	19.69	5.26	0.0379	
BC	16.01	1	16.01	4.27	0.0577	
Curvature	8.15	1	8.15	2.18	0.1623	significant
Residual	52.44	14	3.75			
Cor Total	348.23	20				

Fig. 4.26 Half normal probability plot of percentage of naphtha in liquid product from catalytic cracking of waste chicken fat on coal fly ash in continuous reactor.

The normal plot of residuals shows in Fig. 4.27. The Data should be linear while non-linear pattern such as an S-shaped curve indicates abnormality in terms. The result shows the linear relationship, the R-Squared statistics near for 1 ($R^2 = 0.9773$). The optimum percentage of naphtha yield is calculated by equation 4.30.
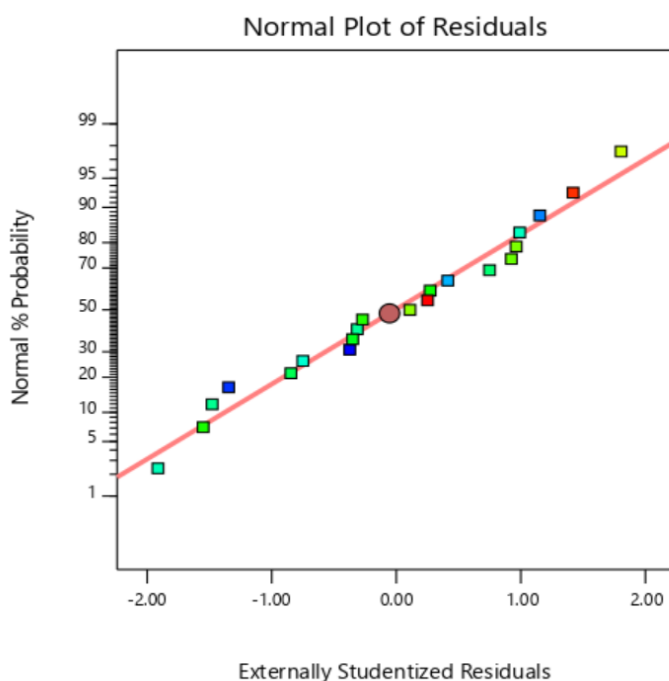
Fig. 4.27 Normal plot of residuals of percentage of naphtha in liquid product from catalytic cracking of waste chicken fat on fly ash in continuous reactor.

$$\text{Percentage of naphtha yield} = +0.54625 + 0.017969 \times A - 8.40125 \times B$$
$$-0.035944 \times B + 0.18442 \times D + 0.018490 \times A \times B$$
$$+0.006668 \times B \times C \qquad (4.30)$$

4.7.3 Percentage of diesel in liquid product

The study of catalytic cracking of waste chicken fat on coal fly ash catalyst using 2^4 factorial experimental designs and the experiment at an average value as shown in Table 4.30, it is found that percentage of diesel yield of 34.38-50.94 %wt.

Table 4.31 shows an ANOVA analysis of variables affect the percentage of diesel in liquid product, it is observed that the main variables A, B, C, D, BC, BD, CD, BCD are significant variations. Half normal probability plot of percentage of diesel in liquid

product as shown in Fig 4.28., it is observed the significant variables deviate from the line.

Table 4.30 Percentage of diesel in liquid product from catalytic cracking of waste chicken fat on coal fly ash in continuous reactor.

|	Factor				%yield of Diesel		Factor Level	
							Low (-)	High (+)
Run	A	B	C	D				
1	420	3	50	30	50.94	A (°C)	420	460
2	460	3	50	30	48.44	B (ml/min)	3	9
3	420	9	50	30	47.56	C (ml/min)	50	150
4	460	9	50	30	43.75	D (V/V)	30	60
5	420	3	150	30	49.69			
6	460	3	150	30	46.25			
7	420	9	150	30	46.88			
8	460	9	150	30	43.44			
9	420	3	150	60	48.13			
10	460	3	50	60	46.38			
11	420	9	50	60	44.94			
12	460	9	50	60	42.81			
13	420	3	150	60	48.13			
14	460	3	150	60	45.88			
15	420	9	150	60	39.38			
16	460	9	150	60	34.38			
17	440	6	100	45	17.03 43.63			

Table 4.31 ANOVA of variables affecting on percentage of naphtha in liquid product from catalytic cracking of waste chicken fat on coal fly ash in continuous reactor.

| Source	Sum of Squares	df	Mean Square	F Value	p-value	
Model	550.39	6	91.73	418.55	< 0.0001	significant
A-Temp	36.97	1	36.97	78.49	< 0.0001	
B-Feed rate CF	103.44	1	103.44	219.58	< 0.0001	
C-Feed rate N_2	22.40	1	22.40	47.55	< 0.0001	
D-Catalyst	45.33	1	45.33	96.23	< 0.0001	
BC	7.63	1	7.63	16.21	0.0020	
BD	11.08	1	11.08	23.51	0.0005	significant
CD	6.33	1	6.33	13.43	0.0037	
BCD	15.87	1	15.87	33.68	0.0001	
Curvature	12.46	1	12.46	26.44	0.0003	
Residual	5.18	11	0.4711			
Cor Total	266.70	20				
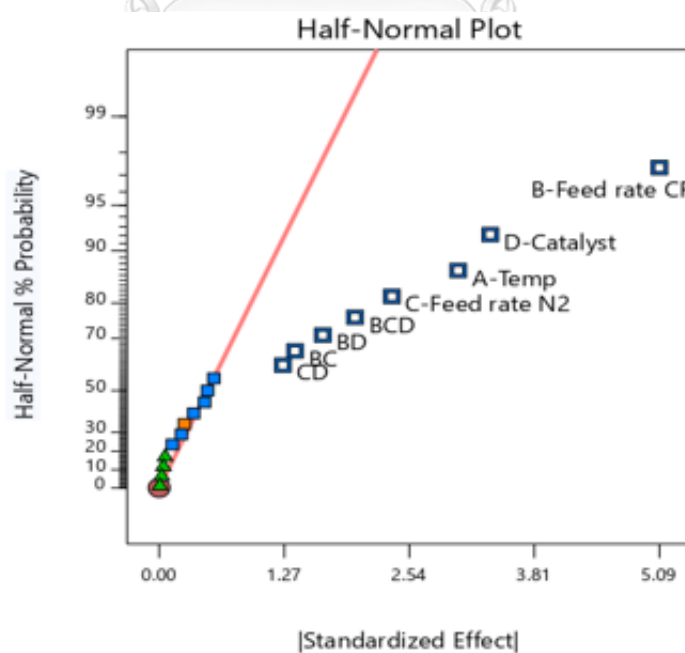
Fig. 4.28 Half normal probability of percentage of diesel in liquid product from catalytic cracking in continuous reactor .

The normal plot of residuals of diesel yield in liquid product from catalytic cracking as shown in Fig. 4.29. A normal probability plot of residuals can be used to check the normality assumption. If the residuals plot approximates a straight line, then the normality assumption is satisfied. It is found the straight line of the residuals percentage of diesel yield. The optimum percentage of diesel yield is shown in equation 4.31.
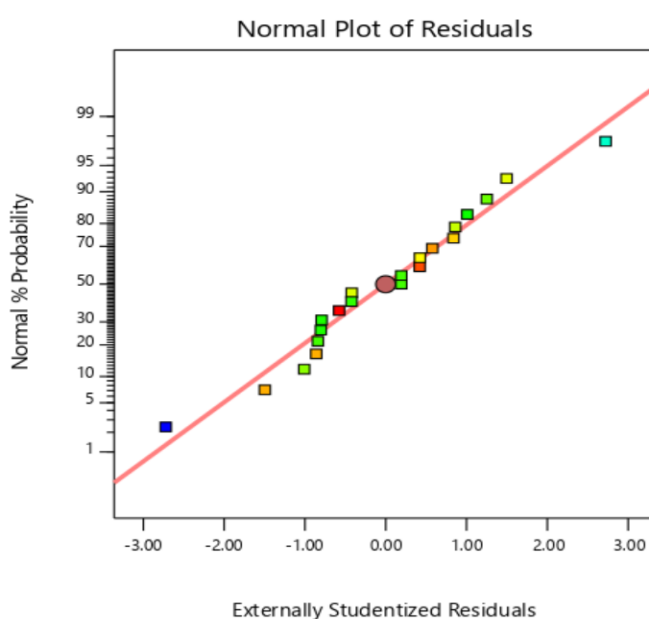

Fig. 4.29 Normal plot of residuals of percentage of diesel in liquid product from catalytic cracking of waste chicken fat on coal fly ash in continuous reactor.

$$
\begin{aligned}
\text{Percentage of naphtha yield} =\ & +91.80000-0.076008\times A-1.54656\times B \\
& -0.077794\times C\ 0.18297\times D \\
& +0.015310\times B\times C+0.025767\times B\times D \\
& +1.81687E\text{-}003\times C\times D \\
& -0.0044256\times B\times C\times D \qquad\qquad (4.31)
\end{aligned}
$$

4.8 The optimum condition of catalytic cracking of waste chicken fat on fly ash in continuous reactor

Program of Design Expert version 11.0.0, which is software for the design of experiments, is used to analysis of the optimum condition. The ranges of variables in Table 4.32 shows the optimum condition. In this research, three responses are mainly considered as follows: percentage of liquid product, percentage of naphtha yield and percentage of diesel yield. Liquid and oil composition are set at the maximum. Afterward, Design-Expert software will calculate the optimum condition.

Table 4.32 The range of optimum condition from Design-Expert program of catalytic cracking of waste chicken fat on fly ash in continuous reactor.

| Variables	Goal	Lower Limit	Upper Limit
Temperature	in range	420°C	460°C
Feeding rate	in range	3 ml/min	9 ml/min
N_2 flow rate	in range	50 ml/min	150 ml/min
Catalyst content	in range	30%V/V	60%V/V
Percentage of liquid product	maximize	44.70%wt	83.39%wt
Percentage of naphtha yield	maximize	8.75%wt	24.81%wt
Percentage of diesel yield	maximize	34.37%wt	50.93 %wt

Table 4.33 shows the optimum condition program from the Design-Expert program compared with the experiment. The optimum condition is the temperature of 460°C, feeding rate of 9 ml/min, N_2 gas flow rate of 50 ml/min and catalyst content of 60 %V/V and give a percentage of liquid product, naphtha yield and diesel yield of 69.44 %, 21.62 % and 41.65%, respectively.

Table 4.33 The optimum conditions of catalytic cracking of waste chicken fat on fly ash in continuous reactor. Between Design-Expert program and the actual experiment.

Variables	Optimum condition	
	Design Expert Program	Actual Experiment
Reaction temperature	460°C	460°C
Feeding rate	9 ml/min	9 ml/min
N_2 gas flow rate	50 ml/min	50 ml/min
Catalyst content	60%V/V	60%V/V
Percentage of liquid product	68.76%wt	69.44%wt
Percentage of naphtha yield	22.21%wt	21.62%wt
Percentage of diesel yield	42.35%wt	41.65%wt

4.8.1 Used fly ash catalyst

The efficiency of the coal fly ash catalyst is studied by deploying the used catalyst in continuous reactor under the optimum reaction condition. The yield of liquid products is analyzed for the catalytic performance as shown in Fig. 4.30. Fly ash is investigated at 9 hours. At the first hour, yield of liquid is 38.29 %wt. It is 65.58 %wt. at 4 hours and remaining constant until 7 hours. After that, the yield of liquid gradual decreases at 8 and 9 hours. As the result, the fly ash can usability for several times. After reaction, fly ash is examined by XRD and BET. Fig 4.31 illustrates the structure of fresh fly ash and used fly ash. The peak of CaO and Fe_2O_3 are replaced a $Ca(OH_2)$ and Fe_3O_4 respectively. CaO is easily deactivated by carbon dioxide (CO_2) and moisture (H_2O) because it adsorbs the catalyst surface and low yield of liquid due to catalyst surface hydration as shown in equation 4.32 [74].

$$CaO + H_2O \rightarrow Ca(OH_2) \qquad (4.32)$$
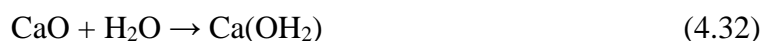
I. Rossettia et al.[75] study deactivation of the catalyst in dehydrogenation of ethylbenzene. The evidence shows the active phase is Fe^{3+} in form of Fe_3O_2. The yield of production is reduced because Fe^{3+} decreases to Fe^{2+}. In this work also finds the same pattern.

Furthermore, the higher of residence time in reaction improves the coke formation. Coke produces from thermal or catalytic cracking from the polycondensation of heavy hydrocarbon and polymerization of Olefin. The coke formation limits the use of catalyst. The deactivation can explain that the coke accumulates within the catalyst pores, therefore, the effective of the catalyst decreases. According to the theory, this research shows the decreasing of surface areas and pore volume after reaction in Table 4.34. It can conclude that the higher reaction time will decrease the performance of coal fly ash
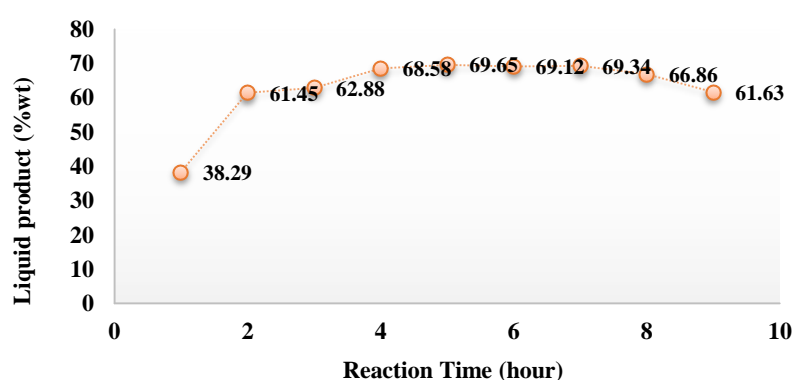

Fig. 4.30 The yield of liquid products of continuous reactor at optimum condition, reaction time on 9 hour.
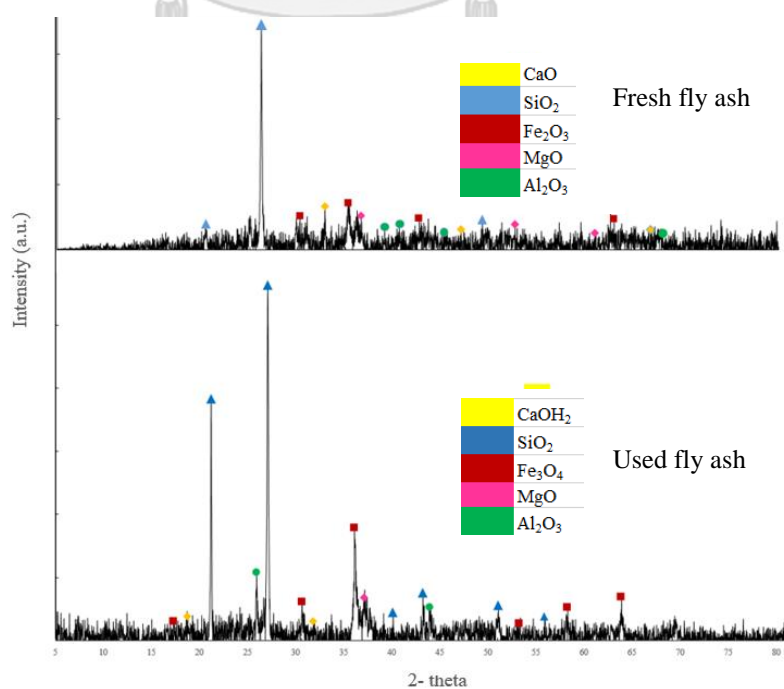

Fig. 4.31 XRD pattern of fresh coal fly ash and used coal fly ash.

Table 4.34 Presented surface area and pore volume of coal fly ash catalyst.

Surface area and pore volume of coal fly ash catalyst			
	Before calcination	calcination 600 ˚C 1hour	After reaction
Surface area (m^2/g)	1.80	2.20	1.92
Pore volume (cm^3/g)	0.0094	0.0100	0.0085

4.9 The effect of variables study for the catalytic cracking of waste chicken fat over coal fly ash catalysts.

4.9.1 The effect of temperature

The effect of temperature on a percentage of the product yield from the catalytic cracking of waste chicken fat over fly ash catalysts in a continuous reactor as shown in Fig. 4.32. At higher temperature increased percentage of liquid product from 55.35 %wt. to 64.18 %wt., because of long chain hydrocarbons are cracked into large amount of medium and small hydrocarbon products. The main factor in cracking process is temperature, the mechanisms of thermal cracking rapidly decompose of triglycerides. Decarboxylation and decarbonylation of heavy oxygenated compounds can occur before or after the C–C bond scission and the free radical decompose of heavy oxygenated compounds. At higher temperatures, cracking occurs, continues producing short chain hydrocarbons, it can observe that higher percentage of liquid product. The effect of temperature on the naphtha yield as shown in Fig. 4.33, the temperature increased from 420 °C to 460 °C, percentage of liquid product increased from 18.44%wt. to 24.82 %wt. The temperature had raised, thermal cracking within system could thoroughly occur, large hydrocarbon molecules cracked into medium hydrocarbon molecules. After that the catalyst played a role in the selectivity to produce small hydrocarbon molecules like naphtha, which resulted in a higher percentage of naphtha yield. Due to the role of surface area and porosity of coal fly ash also affected the hydrogen transfer and occurred hydrogenation reaction. The pore size of catalyst selects the proper size chain such that the yield of naphtha also increases.
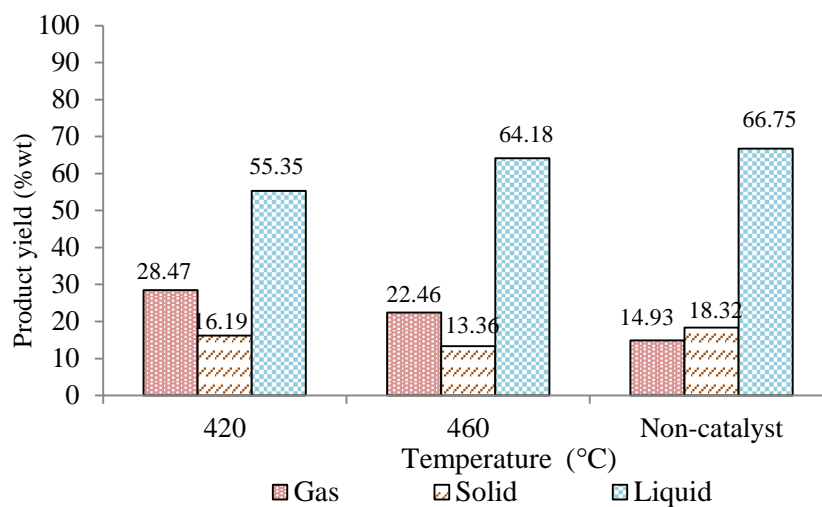
Fig. 4.32 The effect of temperature on product yield in continuous reactor at Feeding rate 9 ml/min, N₂ gas flow rate 150 ml/min, Catalyst content 60% V/V.
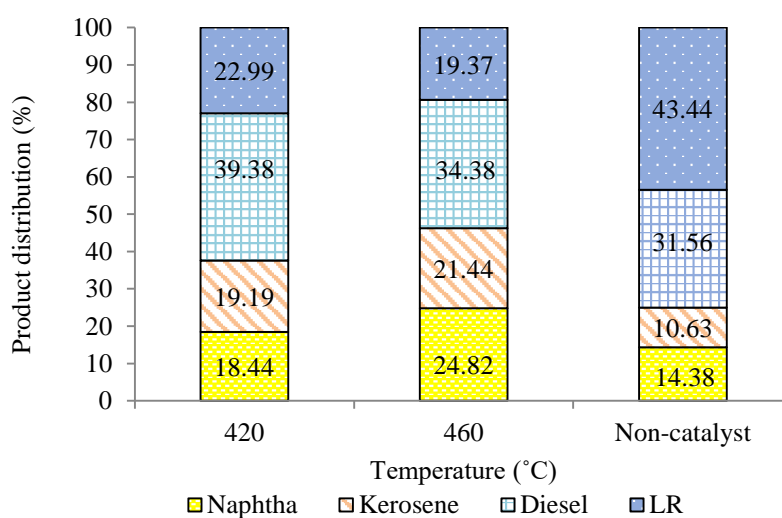

Fig. 4.33 The effect of temperature on product yield in continuous reactor at Feeding rate 9 ml/min, N₂ gas flow rate 150 ml/min, Catalyst content 60% V/V.

4.9.2 The effect of feeding rate

Fig. 4.34 show the effect of feeding rate of waste chicken fat on percentage of product yield from the catalytic cracking process over coal fly ash catalyst in continuous reactor. The percentage of gas yield tend to be increased when increasing feeding rate of waste chicken fat. Reactor can provide enough heat for reactants which promote the cracking reaction. The higher crack of waste chicken fat directly affected to free

radicals, the increasing of the amount of free radical can be cracked further and give a higher percentage of gas yield. The effect of feeding rate of waste chicken fat on percentage of naphtha in liquid product as shown in fig 4.35, it indicates that percentage of naphtha increased from 17.37 %wt. to 24.81%wt. Therefore, the increasing oil feeding rate increases the amount of reactants which provide in better the cracking reaction.

Fig. 4.34 The effect of feeding rate of oil on product yield in continuous reactor at Temperature 460 ˚C, N_2 gas flow rate 150 ml/min, Catalyst content 60%V/V.
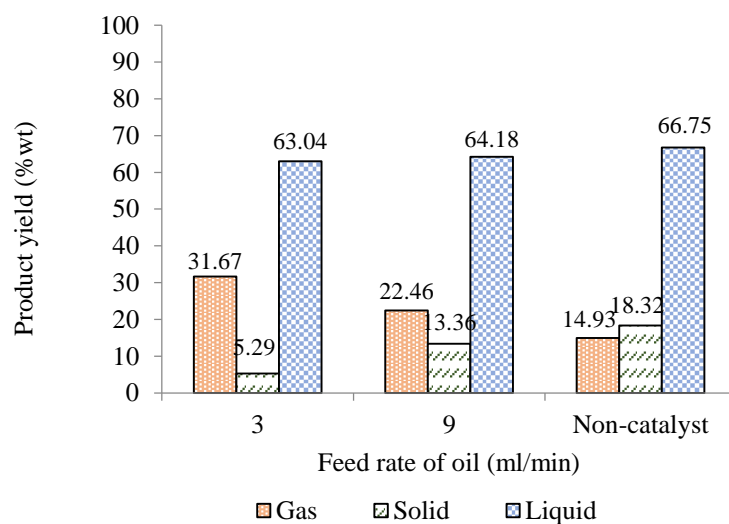
Fig. 4.35 The effect of feeding rate of oil on product yield in continuous reactor at Temperature 460 ˚C, N_2 gas flow rate 150 ml/min, Catalyst content 60%V/V.
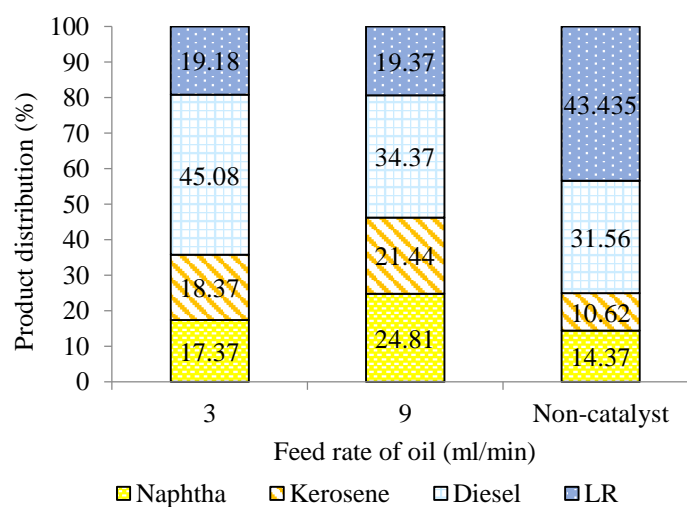
4.9.3 The effect of N_2 gas flow rate

The effect of N_2 gas flow rate as shown in Fig 4.36. The data found that percentage of liquid product decreased from 69.88 %wt. to 64.18%wt. when increasing of N_2 gas flow rate. It can be explained that when increasing N_2 gas flow rate, it is possible that heavy oil needed some time to be cracked into small hydrocarbon molecules. The increasing N_2 gas flow rate might make heavy oil not completely cracked, percentage of liquid product decreased as shown in Fig. 4.36.

Fig. 4.37 showed the effect of the N_2 gas flow rate on percentage of diesel yield in liquid product, at higher N_2 gas flow rate can decrease percentage of diesel in liquid product. Because it is possible that heavy oil needed some time to be cracked into small hydrocarbon molecules, a short time can provide the lower yield of product in cracking process.
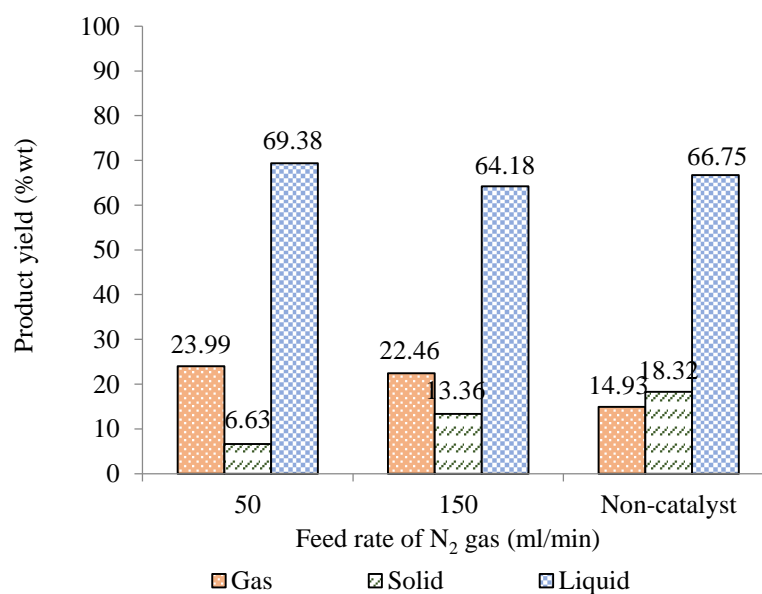

Fig. 4.36 The effect of N_2 gas flow rate on product yield in continuous reactor at Temperature 460 ˚C, Feeding rate 9 ml/min, Catalyst content 60%V/V.
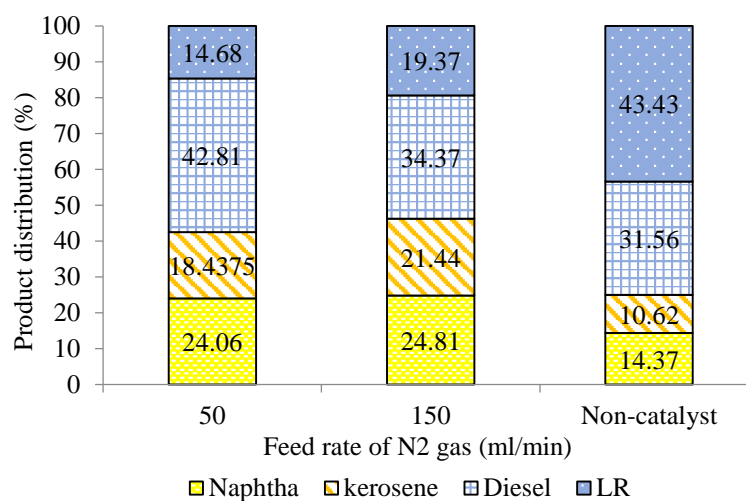
Fig. 4.37 The effect of N_2 gas flow rate on product distribution in continuous reactor at Temperature 460 °C, Feeding rate 9 ml/min, Catalyst content 60%V/V.

4.9.4 The effect of fly ash catalyst

The considering the catalyst content as shown in Fig 4.38. The percentage of liquid product significant decrease from 74.57 %wt. to 64.18 %wt. when increased the catalyst content. It is possible a large coal fly ash content of can make the reaction occur faster, long chain hydrocarbon compounds are cracked into large amount of smaller hydrocarbon compounds. These small hydrocarbons can be further cracked into hydrocarbon gases which resulted in a lower percentage of liquid product as shown in Fig.4.38

Fig.4.39 show the effect of the catalyst content on percentage of naphtha in liquid product, it observes the increasing amount of catalyst can increase the percentage of naphtha in liquid product from 19.06 %wt. to 24.81 %wt. The primary reaction for the cracking of triglycerides start to decompose of a triglyceride into heavy oxygenated components such as a carboxylic acid, ketones, and aldehydes. After the thermal breakdown of the triglyceride molecule, the heavily oxygenated compounds are deoxygenated with decarboxylation and decarbonylation produce heavy hydrocarbon and cracked into paraffins and olefins via thermal and catalytic mechanisms. The catalysts have the functions of both hydrogenation and cracking, the active site of catalyst, act for hydrogen transfer, breaking C-C and C-O bond. It can observe the

increasing of catalyst effect on waste chicken fat can crack into medium hydrocarbon molecules until smaller hydrocarbon molecule. Therefore, the results show a higher yield of naphtha.
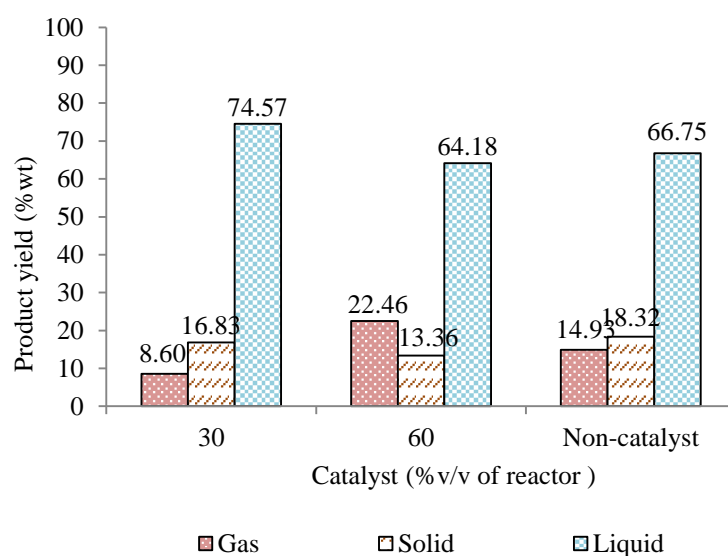

Fig. 4.38 The effect of catalyst content on product yield in continuous reactor at Temperature 460 ˚C, Feeding rate 9 ml/min, N_2 gas flow rate 150 ml/min.
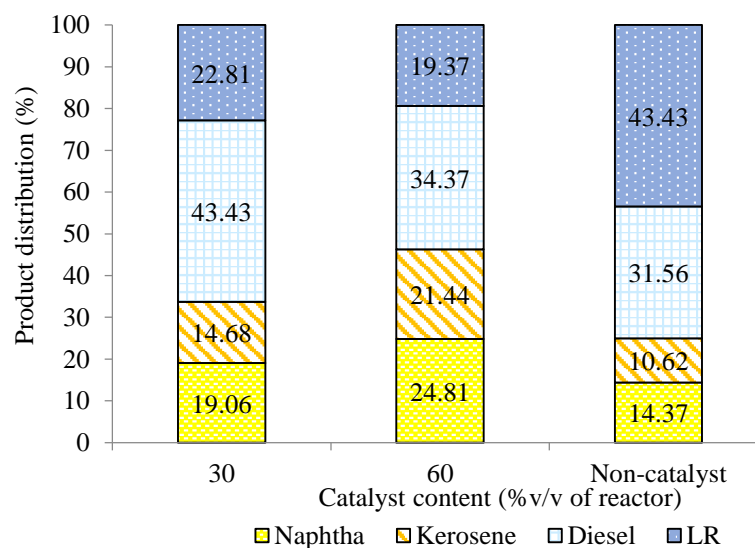

Fig. 4.39 The effect of catalyst content on product distribution in continuous reactor at Temperature 460 ˚C, Feeding rate 9 ml/min, N_2 gas flow rate 150 ml/min.

4.10 Gaseous product analysis

The cracking of waste chicken fat on coal fly ash catalyst is observed from the yield of gaseous products and liquid product. The gaseous products are analyzed by gas chromatograph equipped with a flame ionization detector (FID) and TCD. The experiment data of gas analysis shows that gaseous products consisted of methane (CH4), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2) in Fig.4.40. It proves that the catalytic cracking of waste chicken fat using coal fly ash catalyst in reactor throughs decarboxylation and decarbonylation of free fatty acid and produce CO_2 and CO. Hydrocarbon compounds from decarboxylation and decarbonylation are in the form of paraffins and olefins which will go through cracking. The smaller hydrocarbon compound produces via hydrogen transfer reaction. [64, 65, 71]. The use of catalyst can produce a lower oxygenate in liquid product because the catalyst removes oxygen better than thermal cracking.
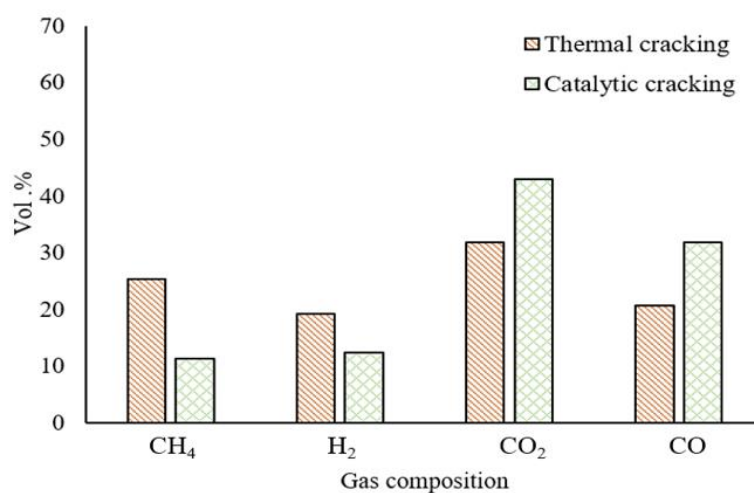

Fig. 4.40 Gas composition from thermal and catalytic cracking.

4.11 Physico-chemical of catalytic cracking of waste chicken fat

The ultimate analysis (C, H, O, N) of liquid fuel which is the analysis of four elements: carbon, hydrogen, oxygen and nitrogen in %wt., it found that the elemental composition of waste chicken fat is 72.52%wt. C, 10.17%wt. H, 16.88%wt. O and 0.43%wt. N. It is also found that the composition of liquid fuel from catalytic cracking in batch reactor has 75.79%wt. C, 11.05%wt. H, 12.75%wt. O and 0.41%wt. N. In addition, the composition of catalytic cracking oil in continuous reactor has 75.72%wt. C, 11.05%wt. H, 12.93%wt. O and 0.30%wt. N as shown in Table 3.35.

In Table 4.35, it can observe the oxygen content is lower the oxygen value of waste chicken fat. It indicates that catalytic cracking of waste chicken fat effectively remove oxygen compound by the way of decarboxylation (produce CO_2) and decarbonylation (produce CO). The decreasing of oxygen content directly affects heating value, when the oxygen content is decreased, the heating value increases. As shown in Table 4.35, it is found that the heating value of liquid fuel increase to 43.39 KJ/kg, while heating value of diesel is between 43.00- 46.00 KJ/kg, which can be nearly the commercial diesel. Therefore, the catalytic cracking oil has better potential to provide heat energy.

The amount of acid value is considerable decrease from 53.30 mg $_{KOH}$/g $_{oil}$ to 13.51 mg $_{KOH}$/g $_{oil}$ in batch reactor, while in continuous reactor the acid value significant decrease to 0.94 mg $_{KOH}$/g $_{oil}$ as shown in Table 4.35. The lower acid value is a benefit which using in transportation fuel. The acidity is the main limitation using bio-oil into a diesel engine, therefore the using of catalyst in cracking process can promote the decreasing of acidity in biofuel.

The viscosity of liquid product from catalytic cracking is close to petroleum diesel, the result of viscosity as shown in Table 4.35. It is dramatically decreased from 68.90 mm^2/s to 3.82 mm^2/s. The viscosity has affected to the efficiency of pump and fuel injection, influence with spay of atomization [12]. The lower viscosity is an advantage, which induces smooth pumping atomization, thus the viscosity need to improve before using in the engine.

Table 4.35 Comparison the physiochemical between waste chicken fat, cracking oil and diesel.

	WCF	Biofuel (this work)		Diesel [66,67]
		Batch	Continuous	
Ultimate analysis				
C (%wt.)	72.52	75.79	75.72	87.17
H (%wt.)	10.17	11.05	11.05	12.76
N (%wt.)	0.43	0.41	0.30	0.07
O (%wt.)	16.88	12.75	12.93	0.00
Fuel Properties				
Hating value (MJ/kg) (ASTM D2015)	39.10	42.96	43.39	43.00-46.00
Viscosity (mm^2/s), at 40 ˚C, (ASTM D445)	68.90	-	3.82	2.00
Acid value (mg $_{KOH}$/g $_{oil}$) (ASTM D664)	53.30	13.51	0.94	No acid value

Fig.4.41 show the chromatogram of liquid product from catalytic cracking of waste chicken fat over a fly ash catalyst at the optimum condition, which the compositions of liquid product are analyzed by gas chromatography-mass spectrometry. The comparison of waste chicken fat with liquid from cracking process is presented, the result of liquid product consists of smaller hydrocarbon, have 10-17 C atoms, the compositions are mainly composed of Cis-9-Octadecenoic acid (C18:1 n-9) and 25.11% Cis-9, 12-Octadecadienoic acid (C18:2 n-6), which had 18C atoms to naphtha and light gas oil. Due to the main effect on cracking process are temperature and reaction time, the increasing of both variables improves cracking of long chain hydrocarbon in waste chicken fat to a smaller chain as a suitable for using in fuel.

These fatty acids are unsaturated substrate, which had double bonds in their molecules. It can observe that the double bond position of fatty acid can be simply degraded. The remove of oxygenate compound is followed by decarboxylation, which produce gas product, CO_2 and hydrocarbon in molecules. Moreover, the oxygen content

of cracking oil is decreased can be cause convent to CO by decarbonylation. In addition, Paraffin and Olefin would occur cracking by hydrogen transfer reaction, that the result in Table 4.36 shows the smaller hydrocarbon molecule in the most of paraffin compound.
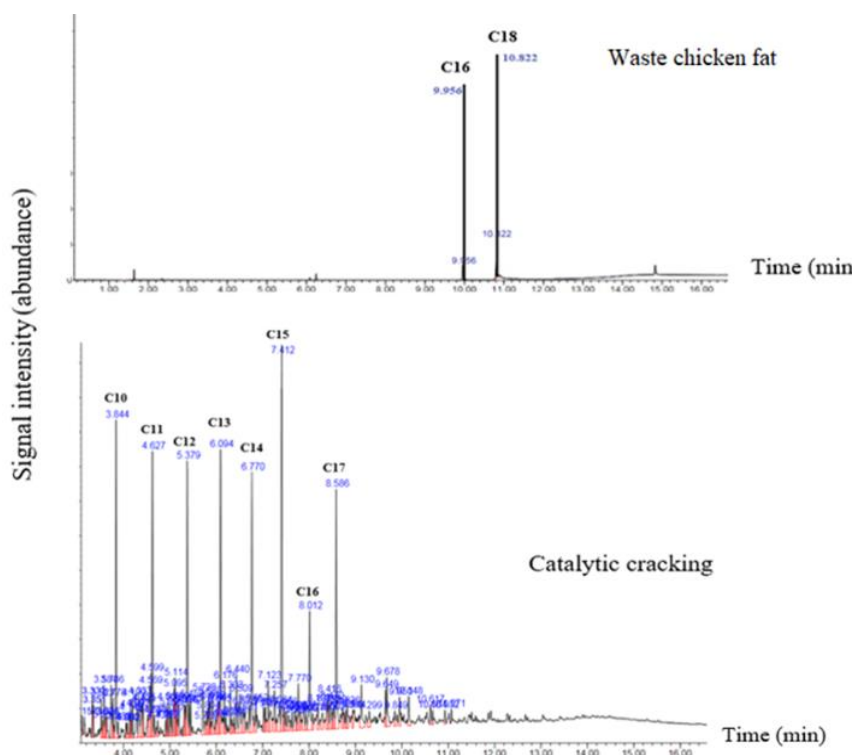
Fig. 4.41 Chromatogram of liquid product from catalytic cracking of waste chicken fat over fly ash catalyst at optimum condition comparing with raw material.

Table 4.36 Main compounds present in the catalytic cracking oil.

Retention time (min)	Area (%)	Compounds
3.845	5.73	Decane
4.626	4.97	Undecane
5.379	5.43	Dodecane
6.095	5.06	Tridecane
6.770	4.98	Tetradecane
7.412	12.11	Pentadecane
8.012	2.70	Hexadecane
8.587	4.76	Heptadecane

CHAPTER 5
CONCLUSIONS AND SUGGESTIONS

The conclusions of this research divided into two sections. The first section is the catalytic cracking of waste chicken fat over coal fly ash catalyst in a batch reactor, the topic consisted of the variables on affecting to liquid fuel and oil composition, optimum condition and kinetics study. The last section is a scale-up of the catalytic cracking into continuous reactor, the results focus on parameters affecting to liquid product and oil yield and determine the optimum condition.

5.1 The conclusion of batch experiment

5.1.1 The variables affecting on percentage of liquid product and oil composition.

Liquid product:

The main variables affecting the liquid yield are temperature (A), reaction time (B), interaction of catalyst content (C) and initial hydrogen pressure (D), interaction of temperature-catalyst content-initial hydrogen pressure (ACD) and interaction of reaction time -catalyst - initial hydrogen pressure (BCD)

Naphtha yield:

The main factors affecting the naphtha yield in liquid product are temperature (A), reaction time (B), catalyst content (C) and initial hydrogen pressure (D), interaction of temperature and catalyst content (AC),and interaction of reaction time -catalyst - initial hydrogen pressure (BCD)

Diesel yield:

The major variables effecting the liquid yield are temperature (A), reaction time (B), and interaction of reaction time -catalyst - initial hydrogen pressure (BCD)

It is observed that the effects of temperature and reaction time are highly significant factor for catalytic cracking process. The increasing temperature and reaction time can cracks a large hydrocarbon into medium and small hydrocarbon molecules. The mechanism consists of free radicals and a carbonium ion from thermal

cracking and catalytic cracking, respectively. Theses reaction continuously cracked until they became a gaseous product. After that, the role of catalyst and the effect of initial pressure has promoted the cracking in reaction.

5.1.2 The optimum condition in a batch reactor

The optimum condition is a temperature of 445 °C, reaction time of 45 minutes, the amount of the coal fly ash catalyst 1 percent by weight and initial hydrogen pressure of 1 bar, at this condition give the highest yield of liquid fuel 76.62%wt, gas 19.54%wt and solid 3.84%wt, respectively. The compositions of liquid fuel are 21.33%wt.gasoline and 31.00%wt. diesel respectively. The oxygen content drop after catalytic cracking process from 16.88 %wt. to 12.75 %wt., which can be caused increase heating value from 39.10 MJ/kg to 42.96 MJ/kg. Moreover, the oxygen content in liquid fuel lower than raw material, coal fly ash catalyst can promote the removing of an oxygen compound by the way of decarboxylation and decarbonylation. The result indicated that CO and CO_2 are the main content in the gas phase, can confirm that the occurring decarboxylation and decarbonylation in reaction. The amount of acid value is considerable decrease from 53.30 mg KOH/g oil to 13.51 mg KOH/g oil, give a benefit which using in transportation fuel.

5.1.3 Kinetics study of catalytic cracking of waste chicken fat over coal fly ash catalyst

The investigation of kinetics study of catalytic cracking of waste chicken fat over coal fly ash catalyst is determined, order of reaction is second order. The study shows kinetics parameter, which are the activated energy 85.97 kJ mol^{-1} and pre-exponential 1.01 x 10^3 s^{-1}.

5.2 The conclusion of continuous experiment

5.2.1 The variables affecting on percentage of liquid product and oil composition.

Liquid product:

The factors affect of percentage of liquid product were temperature (A), feeding rate (B), N_2 gas flow rate (C), catalyst content (D), interaction between reaction temperature and feeding rate (AB), interaction between feeding rate and catalyst content (BD). At the higher temperature, percentage of liquid product is increased, the increasing temperature can raise the energy of reactants, which made waste chicken fat had higher energy and cracked into smaller hydrocarbon compounds.

Naphtha yield:

The variables affecting on percentage of naphtha yield were temperature (A), feeding rate (B), catalyst content (D), Moreover, it was found that the interaction between AB (reaction temperature and feeding rate) and BD (feeding rate and catalyst content). The increasing of feeding rate can increase the amount of reactants, which provide better of the cracking reaction. Additionally, the increasing temperature can promote the cracking of a large hydrocarbon into medium and small hydrocarbon molecules like naphtha, it observes the higher percentage of naphtha yield.

Diesel yield:

The main variables affecting on percentage of diesel yield were temperature (A), feeding rate (B), N_2 gas flow rate (C), catalyst content (D), interaction between feeding rate and N_2 gas flow rate (BC), interaction between feeding rate and catalyst content (BD), interaction between N_2 gas flow rate and catalyst content (CD) and interaction of feeding rate-N_2 gas flow rate-catalyst content (BCD). The increasing of temperature and feeding rate can promote the cracking reaction, which raising of theses reaction produces medium hydrocarbon like a diesel fuel.

5.2.2 The optimum condition in a continuous reactor

The optimum condition is temperature of 460°C, feeding rate of waste chicken fat 9 ml/min, N_2 gas flow rate of 50 ml/min and catalyst content of 60 % V/V and give a percentage of liquid product, naphtha yield and diesel yield of 69.44 %, 21.62 % and 41.65%, respectively. The fuel properties of liquid fuel include heating value, acidity and viscosity. The heating value is 43.39 MJ/kg, it is close to commercial diesel. The amount of acid value is considerable decreased from 53.30 mg $_{KOH}$/g $_{oil}$ to 0.94 mg $_{KOH}$/g $_{oil}$, which the lower of acid value is a benefit for using in transportation fuel. The viscosity in liquid fuel is dramatically decreased from 68.90 mm^2/s to 3.82mm^2/s, near to petroleum diesel is a favourable in diesel engines.

5.3 Suggestions

1. The information of optimum conditions from the experiment in continuous process can be used a guideline for scale-up commercial liquid fuel production in future.

2. The modified coal fly ash catalysts may give better percentage of liquid product, naphtha yield and diesel yield and give lower acid value of liquid product.

จุฬาลงกรณ์มหาวิทยาลัย

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APPENDIX A

The data from batch experiment

Temp/Time /Cat./H₂	Gas	Solid	Liquid	Naphtha	Kerosene	Diesel	LR
420/45/1/1							
average	12.26	3.43	84.63	16.00	11.00	35.50	37.50
420/45/5/1							
average	11.20	5.46	83.35	15.50	12.50	34.00	38.00
420/45/5/5							
average	9.86	5.20	84.95	15.00	11.00	35.00	39.00
420/45/1/5							
average	10.59	4.43	84.99	16.00	12.00	34.00	38.00
420/75/1/1							
average	15.23	3.60	81.18	18.00	12.00	33.50	38.50
420/75/1/5							
average	12.08	4.49	83.44	17.00	11.00	33.50	38.50
420/75/5/1							
average	13.07	6.03	80.91	17.50	12.00	33.50	37.00
420/75/5/5							
average	14.66	5.53	79.82	18.00	12.00	32.50	37.50
460/45/1/1							
average	22.53	6.39	71.08	29.00	14.00	27.50	29.50
460/45/1/5							
average	27.74	7.06	65.20	29.50	14.00	27.50	29.00
460/45/5/1							
average	25.36	9.38	65.06	28.00	14.00	27.00	31.00
460/45/5/5							
average	24.89	6.70	68.42	26.00	14.00	27.50	32.50
460/75/1/1							
average	29.04	7.43	63.54	32.00	14.50	25.50	28.00
460/75/1/5							
average	28.60	7.56	63.85	30.00	14.00	26.50	29.50
460/75/5/1							
average	29.44	8.36	62.20	29.00	14.50	27.00	29.50
460/75/5/5							
average	27.15	5.76	67.10	28.50	14.50	27.00	30.00
440/60/3/3							
average	13.96	5.12	80.91	23.80	13.60	29.80	32.80

The data from continuous experiment

Temp	ไข่ไก่	N_2	Cat. fly ash	% Naph-tha	% Kero-sene	% Die-sel	% Long residue	เฉลี่ย liquid	เฉลี่ย solid	เฉลี่ย gas
420	3	50	30	11.56	9.69	50.94	27.81	58.76	8.23	33.02
460	3	50	30	15.00	11.56	48.44	25.00	71.93	3.55	24.51
420	9	50	30	10.81	11.13	47.56	30.50	78.04	12.22	9.74
460	9	50	30	13.88	14.94	43.75	27.44	83.36	8.02	8.62
420	3	150	30	8.75	10.63	49.69	30.94	55.62	11.20	33.18
460	3	150	30	13.75	12.50	46.25	27.50	70.65	8.86	20.49
420	9	150	30	9.56	9.50	46.88	34.06	70.91	19.25	9.84
460	9	150	30	19.06	14.69	43.44	22.81	74.57	16.83	8.60
420	3	50	60	16.88	15.00	48.13	20.00	54.65	4.00	41.35
460	3	50	60	17.19	14.06	46.38	22.38	67.24	2.86	29.90
420	9	50	60	13.50	12.69	44.94	28.88	61.94	9.12	28.94
460	9	50	60	24.06	18.44	42.81	14.69	69.38	6.63	23.99
420	3	150	60	14.38	11.56	48.13	25.94	44.70	7.91	47.39
460	3	150	60	17.38	19.38	45.88	19.81	63.04	5.29	31.67
420	9	150	60	18.44	19.19	39.38	22.99	55.35	16.19	28.47
460	9	150	60	24.82	21.44	34.38	19.37	64.18	13.36	22.46
440	6	100	45	16.38	18.00	43.13	22.49	59.48	9.44	31.08
440	6	100	45	15.50	19.88	43.75	20.87	57.82	10.56	31.62
440	6	100	45	14.50	17.88	43.75	23.88	53.82	11.04	35.14
440	6	100	45	20.00	16.88	44.38	18.75	56.60	8.98	34.42
440	6	100	45	18.75	15.00	43.13	23.13	56.39	9.57	34.04

APPENDIX B

The use of Design Expert program.

Two-level factorial experimental design is commonly used in experiments involving many factors which aimed to study the interaction that affect the effects of such factors. The most important factorial experimental design was in case of k factors which each factor consists of 2 levels. Each level was due to quantitative data such as temperature, pressure or time, for example or due to qualitative data such as machines or workers, for example. In these 2 levels represent "high" or "low" values of factor or represent "present" or "absent" of factors. In one complete replicate of this design consists of in total of 2×2×2...×2 = 2k data. This design is called 2k factorial experimental design which is very useful for the experiment in the first period when there are many factors that need to be studied. This design can reduce the number of trials in order to study the effect of k factors completely by using 2-level factorial design. It is therefore not surprising that this design has been used widely to filter and to reduce the number of factors. This is each factor of factorial design consists of 2 levels. The responses are linear over the range of factor level studied which the hypothesis is acceptable for the experiment aimed to use factors in studying the system. The study of interaction revealed the effects of factors in Latin capital letters. A represented the effect of factor A, B represents the effect of factor B and AB represented the interaction of factor AB. In 22 factorial design low and high levels of factors were represented by + and – on A and X axis, respectively. For the experimental design with 4 factors they were represented by lowercase letters. High level of any factor was represented by lowercase letter of that factor. For low level, there was no letters presented in the study of interaction effect. Therefore, for this 2k design a represented the interaction effect of high A and low B, b represented interaction effect of low A and high B, ab represented both high A and high B and (1) represented both low A and low B.

Equation for calculation : Contrast was the sum of experimental values of each treatment multiplied by co-efficient (-1 or +1) of factors of the interaction between factors.

From ANOVA analysis using Design Expert the mathematical equation was obtained as shown in equation (D.1). This equation showed the relationship between %yield of liquid and factors and equation (D.2) showed the relationship between diesel fraction in liquid product and factors.

Design Expert: Design Expert version 11.0.0 was used in this study with the procedures from designing the experimental to calculation as followed:

1. Choosing model and defining variables for designing the experimental.

Enter the program, click File --> New Design, the display will show as figure1 Select the model according to the variables to be studied. In this study 4 variables were studied so 2^k level model was chosen.
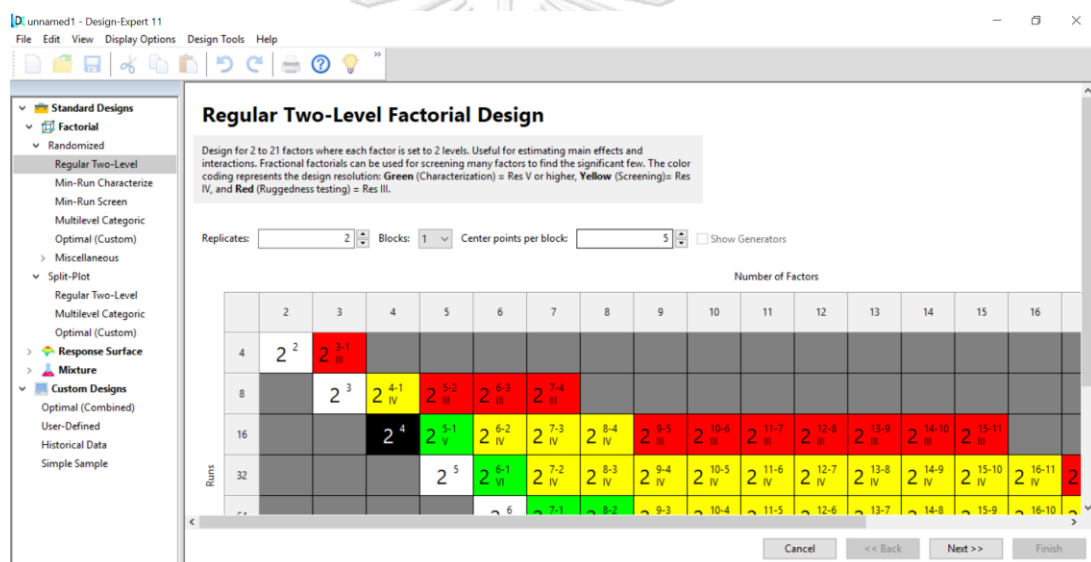
Fig. 1 The table of 2 level factorial design.

b. Choose the option as Fig.1 the display will show as Fig.2 fill the following data. Fill the name of variable in Name. Fill unit of variable in Units. Fill lower value of variable in Low.Fill higher value of variable in High.
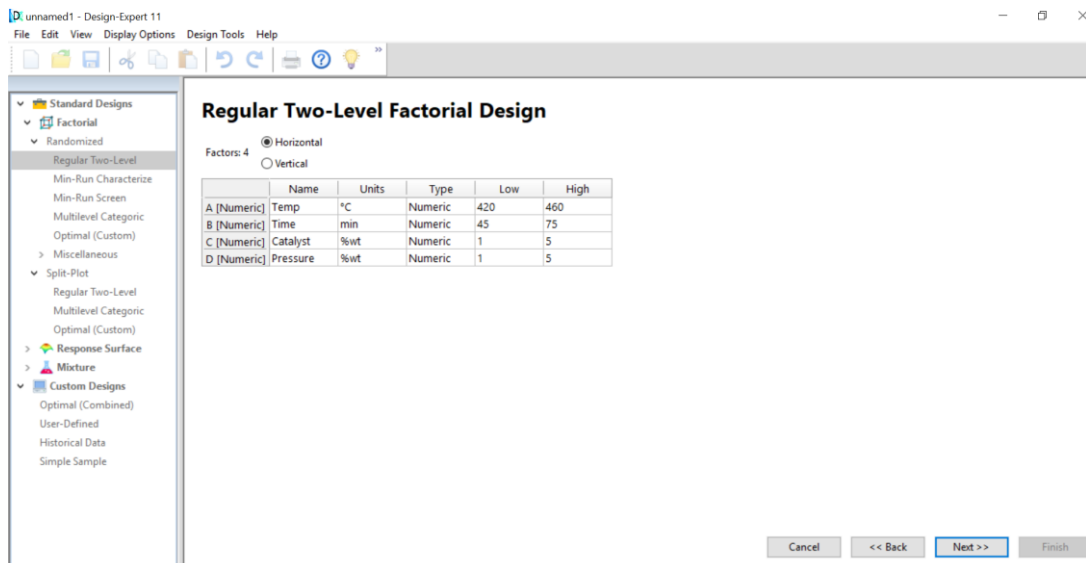
Fig.2 The variables determining

Click Continue, the display will show as Fig.3 Choose the number of responses and fill the name as well as unit of response and click Continue.
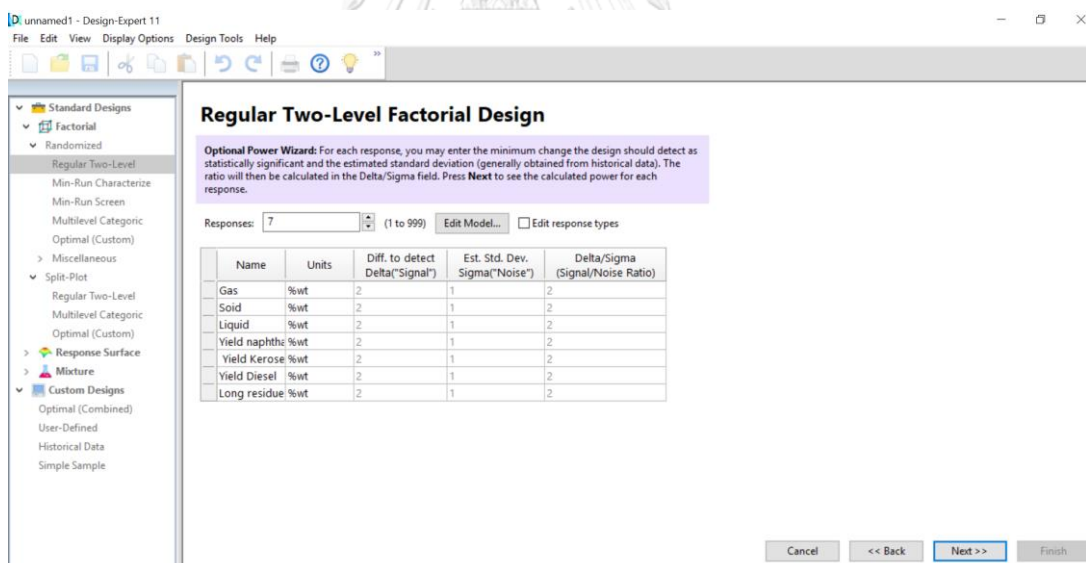
Fig. 3 The responses determining

After setting the value as Fig.3, the software will display a table as shown in Fig.4, this table consists of the sequence of trial, variable value in each trial and blank for defining responses from the experiment. After all trials are performed and response values are defined, the next step is analyzing the experimental results.

Fig. 4 The number of trials and variables of each experiment.

Result analysis begin from choosing responses to be analyzed in left panel and click Effects as shown in Fig.5 Choose the point that deviate from linear relationship.
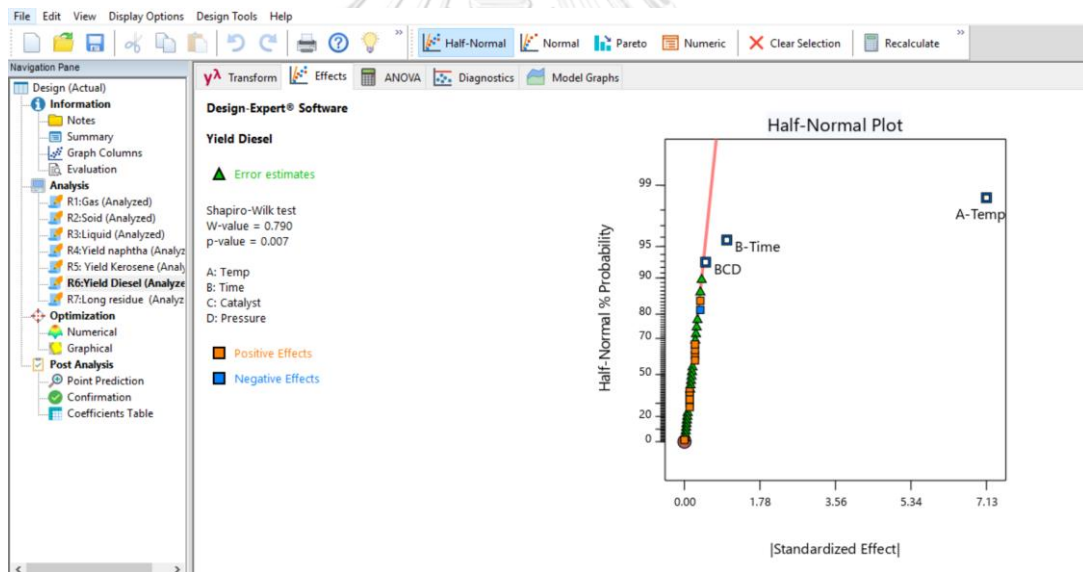

Fig. 5 Half normal plot

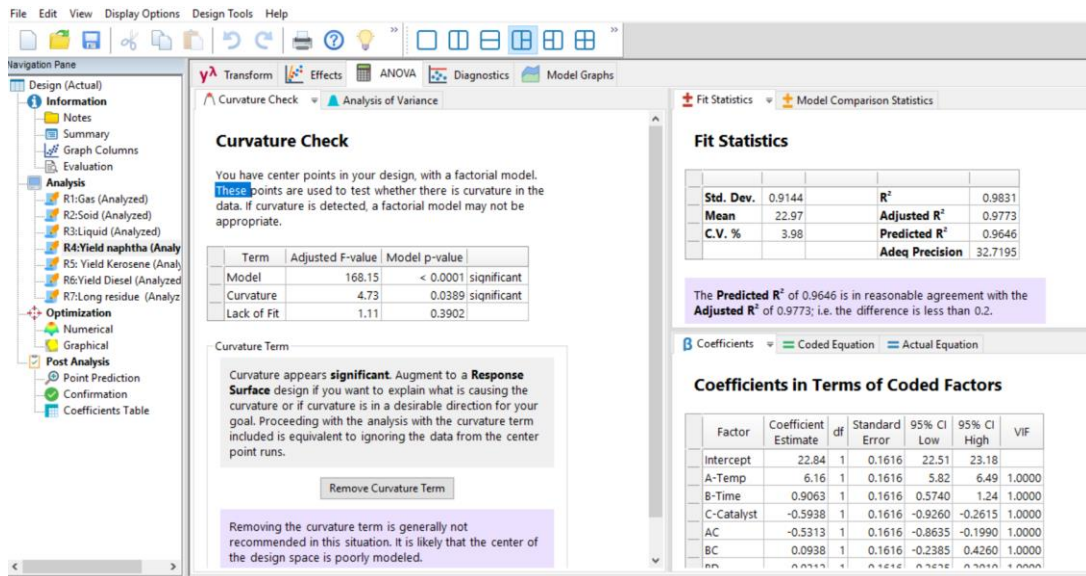Click ANOVA, the table as shown in Fig.6 which present the analysis from ANOVA according to for all responses.

Fig.6 ANOVA analysis of variables.

After all responses are analyzed, the next step is to fine the optimum condition. Select Numerical at the bottom of Optimization in left panel as shown in Fig.7. Define the values of responses such as maximum. Then click Solution it will show the table from the calculation for optimum condition as shown in Fig.8.
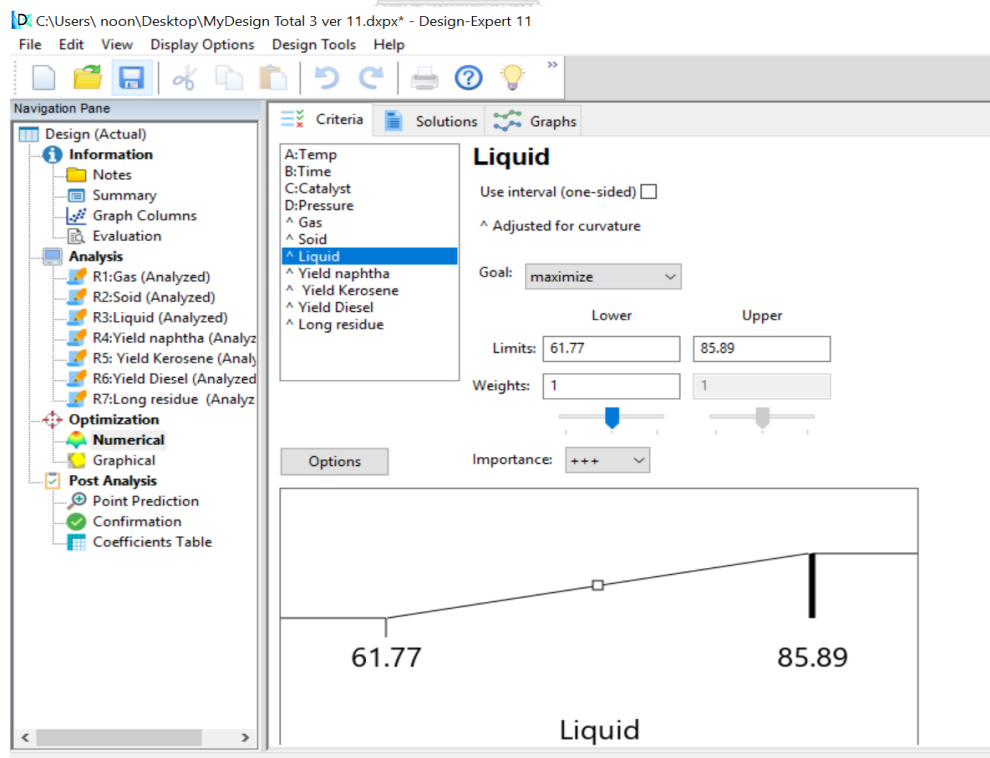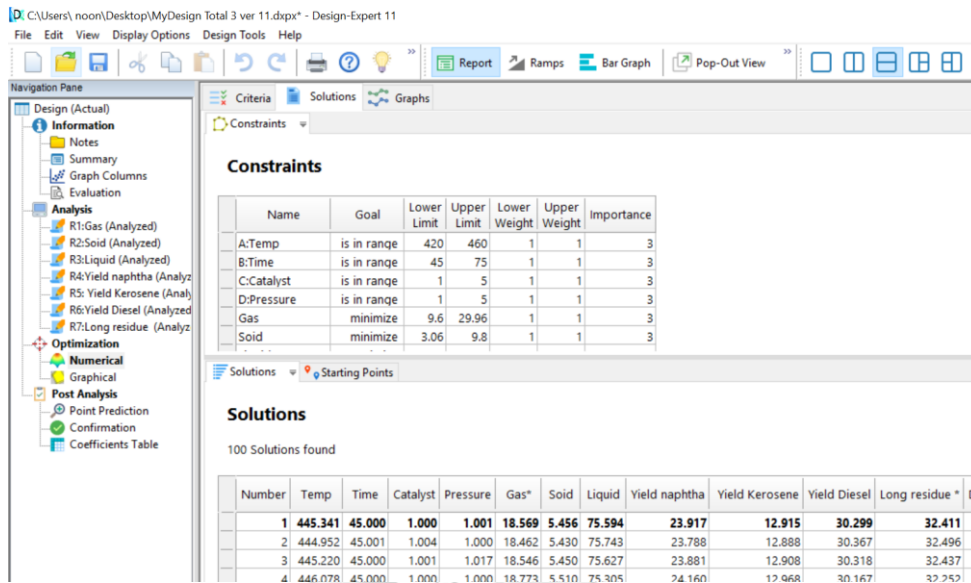

Fig.7 The responses determining for optimum condition.

Fig.8 The calculation for optimum condition.

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