STATISTICAL OPTIMIZATION TRANSESTERIFICATION OF WASTE COOKING OIL (WCO) TOWARDS HIGH QUALITY POLYOLS

This report is submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Hons.)

by

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I hereby, declared this report entitled “Statistical Optimization Transesterification of Waste Cooking Oil towards High Quality Polyols” is the result of my own research except as cited in references.

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Date : 1 JULY 2020

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Hons). The member of the supervisory committee is as follow:

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ABSTRAK

Semenjak kebelakangan ini, kesedaran mengenai potensi dalam minyak masak sisa sebagai produk sisa yang berharga disahkan apabila sebahagian besar kajian sebelumnya menilai produk sisa minyak masak menjadi produk kekayaan seperti biodiesel oleh pelbagai jenis sumber minyak masak sisa seperti sisa minyak sayur-sayuran minyak biji rap atau (RBDPO) Minyak Kelapa Sawit yang di rawat melalui kaedahpelunturan. Penggunaan minyak masak sisa mulai berkembang kerana isu penipisan sumber semula jadi dan isu pelupusan sisa minyak masak sisa di mana ia secara signifikan menyumbang kepada pencemaran alam sekitar dan kesan jangka panjang. Selanjutnya, menyedari bahawa potensi WCO dalam menghasilkan poliol sumber semula jadi menyebabkan penyelidikan ini memanipulasi kebergantungan pemboleh ubah dalam proses transesterifikasi untuk menghasilkan poliol berkualiti tinggi yang dapat ditentukan oleh kehadiran kumpulan hidroksil (OH-) di struktur molekul kerana semakin tinggi kuantiti kumpulan hidroksil dalam struktur molekul, semakin tinggi kualiti poliol. Walau bagaimanapun, kajian ini menggunakan kaedah statistic analisis dengan menggunakan data dari kajian sebelumnya dengan secara khusus dari proses transesterifikasi untuk memperkenalkan kumpulan OH dalam struktur trigliserida WCO sehingga terbentuk persamaan yang sah. Persamaan yang sah digunakan untuk memanipulasi tiga parameter iaitu kepekatan NaOH, nisbah Metanol ke minyak dan suhu untuk mendapatkan poliol berkualiti tinggi. Berdasarkan hasil dari persamaan yang sah, analisis statistik pada reka bentuk faktorial dua tahap lengkap dilakukan untuk menilai kesan parameter dan kehadiran kumpulan OH oleh (DOE) sebuah perisisan statistikal reka bentuk kajian. Kepentingan simulasi pemodelan dari reka bentuk faktorial dua tahap disahkan melalui analisis ujian ANOVA dan kerana ia signifikan, ia meneruskan penilaian interaksi antara parameter. Akhir sekali, kajian ini juga melakukan pengoptimuman parameter melalui analisis kesan dan interaksi di antara pemboleh ubah bebas.

ABSTRACT

Over these recent years, awareness of potential in waste cooking oil as a valuable waste product are confirmed when most of the previous research evaluating waste product of cooking oil into wealth product such as biodiesel by different types resources of waste cooking oil such as waste of vegetables oils, rap seeds oil or (RBDPO) Refined Bleached Deodorized Palm Oil. Utilizing of waste cooking oil is starting to develop due to the issue on depletion of the natural resources and waste disposal issue of waste cooking oil where it significantly contributed into environmental pollution and a long-term effect. Furthermore, realizing that the potential of WCO in producing a natural based resources polyol led this research to manipulated the dependent variables in transesterification process to produce a high-quality polyol which can be defined by the presence of the (OH-) hydroxyl group in the molecular structure due to the higher the quantity of hydroxyl group in the molecular structure, the higher the quality of the polyols. However, this study implementing a statistical analysis by using data from previous literature with specifically from transesterification process to introduce OH- group in triglyceride structure of WCO until a valid equation was form. The valid equation was used for manipulating three parameter which is NaOH concentration, Methanol to oil ratio and temperature to get a high-quality polyol. Based on the result from the valid equation, a statistical analysis on two level full factorial design were perform to evaluate the effect of the parameter and the presence of OH- group by (DOE) Design of Expert statistical software. The significant of the modelling simulation from two level factorial design was confirm via the ANOVA testing analysis and since it was significant, it proceeds with the evaluation of interaction among the parameter. Last but not least, this study also conducting an optimization of the parameter through the effect and interaction analysis among the independent variable.

DEDICATION

Every challenging work needs an effort and support from the guidance.
My earn in this research, I dedicated to
Mr. Yunos bin Untong for earning an honest living, supporting and encouraging,
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AG	-	Acyglycerols
ASTM	-	American society for testing and materials
COD	-	Chemical oxygen demand
DC	-	Dangling chains
DOE	-	Design of experiment
EANC	-	Elastically dynamic system chains
FAME	-	Fatty acid methyl ester
FFA	-	Free fatty acid
FTIR	-	Fourier transform infrared spectroscopy
g-PU	-	Green polyurethane
MDI	-	Methylene diphenyl diisocyanate
MPOC	-	Malaysian palm oil council
NMR	-	Nuclear magnetic resonance
PTG	-	Polymerised triacyl glycerides
PU	-	Polyurethane
PUFs	-	Polyurethane foams
RSM	-	Response surface methodology
SOP	-	Standard operation procedure
TAG	-	Triglyceride
USD	-	United State Dollar
WCO	-	Waste Cooking Oil

LIST OF SYMBOLS

cm	-	Centimetre
m	-	Metre
%	-	Percent
g/cm^3	-	Grams per centimetre cube
wt%	-	Weight percent
Millimetre	-	mm
MPa	-	Mega Pascal
MHz	-	Mega hertz
°C	-	Degree Celsius
Tg	-	Glass transition temperature
$kg.cm^3$	-	Kilogram centimetre cube
kg	-	Kilograms
mm/min.	-	Millimetre per minute
rpm	-	Revolution per minute
kN	-	Kilo newton
m	-	Mass
v	-	Volume
°C/min	-	Degree Celsius per minute
KOH	-	Potassium Hydroxide
NaOH	-	Sodium Hydroxide
OH^-	-	Hydroxyl group

CHAPTER 1

INTRODUCTION

This chapter consist of background study of this research where the issue of waste cooking oil in disposal management and depletion of hydrocarbon sources that led to the finding of problem statement that clearly explained the needs of this research about transformation of waste cooking oil into a high-quality polyol. Next, research objectives section which stated the target of this research with the method used to tackle the research problems. Followed by scope and significance of study section that explain about the limitation of material, area, method and technology used in the scope section and relevance. Besides, report organization justify the content organization in this thesis. Lastly, a summary of section to conclude the introduction of this research work.

1.1 Research Background

Waste cooking oil are known as a zero-value waste product to community since it way a common product from each households, restaurant or food processing industry. It can be produced by anyone in this world. Previous studies mostly defined waste cooking oil as the oils and fats that have been used in cooking such as frying. Waste cooking oil is a derivation from various type of cooking oil such as vegetable oil, cumin oil, corn oil, palm olein oil and any type of oil that containing a huge number of saturated fatty acids. Referring to the result of investigation from 352 households in awareness, attitudes and practices towards recycling

of WCO conducted in year 2013, it shows that about 2.34 kg/month WCO had been produced per household. According to Anita Ramli and Muhammad Farooq (2015) Malaysia are one of the developing countries that producing a large number of waste cooking oil by generating about 0.5 million ton per year.

A high production of waste cooking oil is a major influence on the pollution problem to environment due to poor management and non-soluble properties of the oil. A poor management led to pollution on land by changing the color of soil, converting the pH to alkaline and deplete the nutrients such as carbon and nitrogen (Kamilah et al., 2013). It also led into water pollution since non-soluble oil layer will avoid the dissolution of oxygen and mixture of oil and water that increased the Chemical Oxygen Demand (COD) of water. Thus, situation caused the poisonous condition due to presence of oil degradation by products. Lacking of awareness on WCO has led into hazardous to human health because repeated used of WCO could generates a toxic compound such as peroxide, aldehyde and polymer via subsequent chemical reaction. However, WCO can be recycled into useful commercial product as WCO have a great potential to be commercialized into the production biodiesel product (Kumaran et al., 2011). WCO also have a potential to be converted into a polyols based polyurethanes and bitumen. In this study, due to great potential application of WCO a circular bio economy action will be taken by converting the WCO into polyols or any other derivatives for various applications, conversion and WCO into polyols for polyurethane could give good impact in polymer industry as we could reduce the dependency towards petroleum hydrocarbon for polyols feedstocks.

Polyols is defined as alcohol or organic compound which has two or more hydroxyl group. Previous studies mostly defined polyols as oligomeric backbone that contain of two or more hydroxyl group. The following Figure 1.1 shows the chemical structure of several polyols type, due to initial presence of fatty acid or methyl ester in their triglyceride structure. Polyols have variety of functional properties such as raw material in production of polyurethane and also can be used as an alternative to sugar in various applications. A high-quality polyol can be characterized by quantifying the number of hydroxyl group available in the structure after the transesterification process of waste cooking oil (WCO) through the

Fourier Transform Infrared Spectroscopy (FTIR) analysis method. In this study, a polymerization of high yield hydroxyl group of polyols and isocyanate will be performed for production of green polyurethane (g-PU). Isocyanate is a raw material for production of all polyurethane products, it also known as compounds that containing the isocyanate group (-NCO) where these group will be reacted with hydroxyl group in polyols for the synthesis of polyurethane polymers.

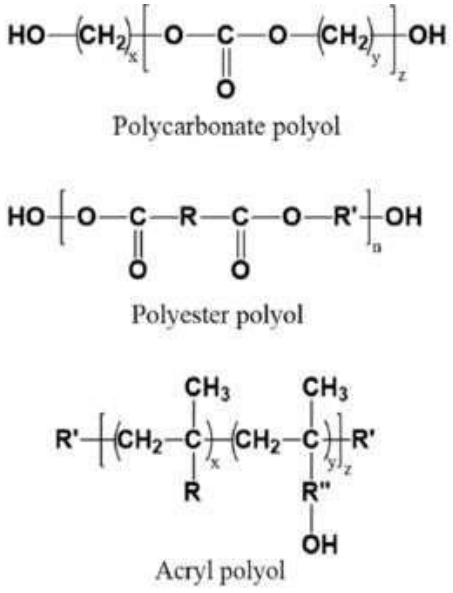

Figure 1.1: Chemical Structure of Polycarbonate Polyol, Polyester Polyol and Acryl Polyol

(Akindoyo et al., 2016)

Transesterification can be broadly defined as a chemical process where exchanging of alkoxy group of an ester compound by another alcohol. Basically, transesterification is where the esters are obtained from the fatty acids and triglycerides of waste cooking oil (WCO) by double processing steps of methanolysis and epoxidation with certain experimental parameter such as the mass of the NaOH solution (g), revolution per minute (rpm), time (min) and temperature (°C). FTIR is a technique utilized for measuring the intensity of infrared radiation as a function of frequency or wavelength. The disappearance of C=C functional group and the presence of hydroxyl group in the structure of polyols occurs along the transesterification process and these can be confirmed by the FTIR analysis where in the literature, the approach is referring to an analytical tool used to examine the type of chemical bond and functional

group appear in WCO and WCO based polyols. Along this research, quantitative analysis of FTIR curves are used in order to gain the insights on hydroxyl group presence and C=C bonds disappearance.

The history of polyurethane is back to the start of World War II, when it was first created as a trade for elastic type material. The adaptability of this new synthetic polymer and its structure to replace expensive raw materials for various applications. Polyurethane application can be seen in daily life. It is the thing that keep food fresh and drinks cold since almost every fridge in the world uses polyurethane as versatile insulating material.

Polyurethanes nowadays are formed by reacting a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polymeric isocyanate, in the presence of suitable catalysts. One purpose of this study, a production of green polyurethane for sustainable polyurethane production. Green polyurethane is made from green source of polyol where the green source is WCO based polyols. From the findings of Economic Benefits of Polyurethanes (2017), most of the industries depend on polyurethane such as building and construction sector, transportation, industry appliances, furniture or even bedding. Polyurethane also support the economic growth of United State by generating about $ 264.1 billion in output and employed more than 1 million workers in other industries.

This research can be best treated under three headings, first the usage of WCO as a green source of based polyols by using the transesterification process and characterized via valid equation from previous literature review. Second, the study of the effects and relationship between the independent variables to the quality of produced polyols by using the statistical design of experiment (DOE) approach. Third, to assess the feasibility of WCO based polyols characteristic as the sustainable base of green polyurethane. The following section was emphasized further the problem statement related for this research work.

1.2 Problem Statement

Recent research has revealed that the source of petroleum was getting depleted and the price fluctuation was substantially increased. This issue has made the petroleum-based polyols was not applicable and sustainable anymore (Tahir et al., 2016). Petroleum-based polyols also has potential in producing pollutants according to non-biodegradability characteristic of them. Petrochemical based polyols also used for making the polyurethane foams are harmful to environment. Hence, these problems has led to the innovation of polyols alternative source to make sure the continues sustainable production of polyurethane with a constant and reasonable price, eco-friendly and sustainable product development.

In previous studies on polyols production, different variables have been found to be influenced the production of polyols from alternative source of feedstock such as vegetable oils, palm oil, sesame seed oil and even waste cooking oil. In line with the massive disposal about 50 000 tons of waste cooking oils are produced in Malaysia as compared than million tonnes that are produced globally (Kheang et al.,2011). This factor made WCO from household becomes relevant as raw material for polyols production. Thus, high quality polyols are required for various application of green polyurethane production by study the WCO based polyols production such as the effects of catalyst concentration into the disappearance of the C=C on structure of WCO and the analysis of OH group presence in polyols structure. This is because at higher OH quantity at methyl ester could make it variable in many applications.

However, the problem had arised when producing a high-quality polyol with higher presence of OH at the backbone of methyl ester structure, an optimization of the parameters used should be clarified such as the temperature and reaction rate to accelerate and enhance the yield of OH and the best concentration will be used in transesterification process. Presence of OH was enhanced in this production because the availability of OH to react with isocyanate to use for many more applications.

1.3 Objectives

The objectives of this research are stated as follows:

I. To determine the relationship between the effects of reaction temperature, methanol to oil ratio and sodium hydroxide concentration (wt%) as independent variables in high quality polyols production by using two level full factorial statistical design approach.

II. To calculate the polyol yield by using a valid equation from previous literature review.

III. To model the simulation calculation result using (Two-Level Factorial approach) DOE statistical software.

1.4 Scopes of Research

The scopes of research are as follows:

I. Using equation from literature review on Waste Cooking Oil conversion into polyols due to methanolysis reaction.

II. Study the effects and relationship between the temperature concentration of NaOH and methanol content towards the presence of hydroxyl group in polyols production by using the DOE software of two level full factorial statistical design approach.

III. Simulated data based on transesterification process and the optimization performed using the simulated data from DOE software.

1.5 Significant of Research

The significance of research could be stated as follows:

Polyols are widely used in polyurethane industry, it become one of the important sources for polyurethane structure due to the ability to diisocyanate depending on their own backbone structure (OH^- group presence). Polyurethanes are very important to industrial or even to ourselves due to various application of polyurethane in our daily life until in industrial, for example from our bedding which made from the PU foam to the insulation used in industrial application or for our refrigerator at home. The wide range usage of polyurethane has led into the depletion of origin source hydrocarbon petrochemical and troublesome issue of nonbiodegradable product.

Hence, it was important to replace the source of polyols to the natural of waste source such as WCO where by using WCO as raw material also could help in the problem solving of recycling the waste cooking oil which contribute to the pollutant. This study was very significant since up till now, there are no similar or available research that establish the relationship between those experimental factors which are the correlation between temperature NaOH and methanol content toward the OH presence at the polyols structure.

1.6 Organization of Report

This report is writing about the research on "Statistical Optimization Transesterification of Waste Cooking Oil towards High Quality Polyols Production" which comprises of five chapter.

Chapter One state the background of the study, problem statement, objectives, scope, study significance, organization and summary of the report. Chapter Two covers the sources of the reference of study where it was about the past study about waste cooking oil, polyols, transesterification and polyurethane. Information in this study may be used in conducting or improving the experiment that will be conducted. Chapter Three generally covered the experimental methodology of this study. From review and comparison in chapter 2, it will strengthen the direction of this research work. In chapter 3, it involves the methodological flow, the flow chart which covers the entire process and equipment used such as the steps and work flow in determined the optimization. Chapter Four shows the overall results and findings with related explanation and analysis, the results will be form in a structured and unstructured data. Finally, Chapter Five covers the conclusion for all research findings. Suggestion and recommendation of any idea for the future research also covered in this chapter.

1.7 Summary

Overall, this chapter highlight the background of this study as the introduction for material, equipment and process involved in this research. Next, problem identifying has been stated clearly that led into the purpose of this research. Generally, this research was consisted of three objectives which are transformation of WCO into polyols and the identification of its potential for production of green polyurethane. The scope and the significant of this research also have been clearly justified to make sure this research is rational and applicable.

CHAPTER 2
LITERATURE REVIEW

Based on the previous study and research, this chapter brings an insightful overview of the structural modification WCO via transesterification for polyols conversion. A fundamental of PU and Polyols discussed in this chapter which includes the structure, types, properties, modification, and the applications. Based on the reference of the previous study, the author will make a comparison of modification and the application applied. Besides the comparison of the changing of the structure with the parameter applied, such as the temperature reaction, catalyst and the concentration used in the experiment. Next, this chapter also studies the methods used for verification and analyzing data obtained during the experiment. This chapter also consists of an implementation of updated technologies such as ANOVA and DOE (two level factorial approach), in the experiment conducted.

2.0 Structural Modification of WCO via Transesterification Process for Polyols Conversion

Waste cooking oil can be marketed as it tends to be utilized in the biodiesel production (Kumaran *et al.*, 2011), polyurethane (polyol) and bitumen (Asli *et al.*, 2012) where it can help the problem of depletion of the natural resource of petroleum. The specialty of structural modification of waste cooking oil led to many findings since the structural composition of cooking oils made up of triglycerides which having a hydrophobic characteristic and consist of three mol of fatty acids with different number of unsaturated bonds, length of the carbon chain and a mol of glycerol (Andrade *et al*., 2014). Thus, it led to the transesterification process for polyols conversion. Transesterification is one of the processes used to acquire esters from fatty acids and triglycerides in sleek sources such as