Faculty of Resource Science and Technology

Characterisation of the Functional Group Properties of Biodiesel and Other Fuel Products

Nurhazirah Binti Basir

(27756)

Bachelor of Science with Honours

Chemistry Resource

2013

DECLARATION

I hereby declare that this thesis entitled “Characterisation of the Functional Properties of Biodiesel and Other Fuel Products” is based on my own research except as cited in the references. The thesis has not been submitted or accepted for any degree.

Signature: ....

Name: Nurhazirah Bt Basir

Date:

ACKNOWLEDGEMENT

Foremost, I would like to express my deep gratitude to Allah SWT for giving me strength and guidance to completing the research studies and make this study possible.

I would like to express my very great appreciation to my supervisor, Dr. Sim Siong Fong for her patience, enthusiastic guidance and useful critiques of this project. Her encouragement and motivation helped me in all time of research and writing of this thesis. I could not have imagined having a better supervisor for my degree study.

Next, I am particularly grateful for the assistance given by my co-supervisor, Dr. Tay Meng Guan for helping me in biodiesel preparation. Besides, my next co-supervisor Dr. Micky Vincent provided me with very valuable information for emulsified biodiesel. Without both of them, I would not be able to prepare my research fuel products and completed my project.

My special thanks are extended to the science officers, laboratory assistants and staff of Faculty of Resource Science and Technology, UNIMAS for their helps along my project work. Last but not least, I would like to offer my special thanks to my beloved parents and friends for their prayers and moral support throughout my study. I will be grateful forever for your love.

Thank you very much.

Table of Contents

List of Abbreviations

ATR-FTIR	Attenuated total reflectance-FTIR
E-biodiesel	Emulsified biodiesel
FA	Fatty acid
FTIR	Fourier transform infrared
IR	Infrared
$MgSO_4$	Magnesium sulphate
Na_2SO_4	Sodium sulphate
NaOH	Sodium hydroxide
O/W	Oil-in-water
TAG	Triacylglycerols
W/O	Water-in-oil

List of Tables and Figures

Characterisation of the Functional Group Properties of Biodiesel and Other Fuel Products

Nurhazirah Bt Basir

Resource Chemistry

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

ABSTRACT

This study attempts to examine the functional groups of various fuel products including biodiesel, emulsified biodiesel (E-biodiesel), petrol and diesel. Biodiesel was prepared for the study from different feedstock by transesterification process in a ratio 1:2 of oil to methanol with 1% w/v of catalyst. E-biodiesel was prepared by further addition of water and surfactant to the biodiesel. Petrol and diesel are commercially available. The fuel products were analysed using Fourier Transform Infrared (FTIR). The transesterification process of biodiesel was confirmed by the presence of the peak at 1196 cm^{-1} showing the characteristic of CH_3-O group. As the E-biodiesel was made from cooking oil, the IR spectrum shows similar pattern of spectra except for O-H band peak. Petrol and diesel are differentiable from biodiesel with petrol sample indicated weaker transmittance band at 1740 cm^{-1} whilst this band is absent in diesel. Additionally, the transmittance bands at lower frequencies, typically in the region of 1300-1000 cm^{-1}, are not found in diesel.

Keywords: Functional groups, various fuel products, characteristic, transmittance band, frequencies

ABSTRAK

Kajian ini bertujuan untuk mengkaji kumpulan berfungsi yang terdapat daripada pelbagai jenis produk bahan api termasuk biodiesel, E-biodiesel, petrol dan diesel. Biodiesel yang disediakan untuk kajian adalah daripada sumber bahan mentah yang berbeza dengan proses transesterifikasi dalam nisbah 1:2 minyak:methanol dengan 1% w/v pemangkin. E-biodiesel telah disediakan dengan menambah air dan 'surfactant' pada biodiesel. Petrol dan diesel boleh didapati secara komersial. Produk-produk bahan api ini telah dianalisis menggunakan 'Fourier Transform Infrared' (FTIR). Proses transesterifikasi biodiesel telah dipastikan dengan kewujudan band pada 1196cm^{-1} yang menunjukkan ciri-ciri kumpulan CH_3-O. E-biodiesel diperbuat daripada minyak masak, spectrum IR menunjukkan corak yang sama pada spectrum kecuali untuk band kumpulan O-H. Petrol dan diesel berbeza daripada biodiesel dengan sampel petrol yang menunjukkan band lemah pada 1740 cm^{-1} manakala bacaan ini tidak terdapat dalam diesel. Tambahan pula, band pada frekuensi yang lebih rendah seperti diantara 1300-1000 cm^{-1}, tidak terdapat dalam diesel

Kata kunci: Kumpulan berfungsi, pelbagai produk bahan api, ciri-ciri, band, frekuensi

1.0 Introduction

The fuel sources are referred to petroleum based products typically diesel and petrol. Over the past few decades, biodiesel has attracted increasing attention as an alternative fuel sources. The name of biodiesel was introduced in the United States in 1992 by the National Soy Diesel Development Board which has pioneered the commercialization of biodiesel (Singh *et al*., 2010). Chemically, biodiesel is produced *via* transesterification of triglycerides with alcohol, commonly methanol, in the presence of base or acid catalyst into fatty acid methyl esters (FAME) (Darwin Sebayang *et al.*, 2010). It is made from renewable sources such as used cooking oil.

Fats and oil are fundamentally composed of triglycerides with varying compositions of saturated and unsaturated fatty acids that serve as a perfect feedstock of biodiesel. Often time, cooking oil is used for the reason that it is environmentally sustainable. The cost of production for biodiesel is cheaper than other raw materials. Zhang *et al.*, (2003) reported that biodiesel has a more favourable combustion emission profile than petroleum-based diesel for example biodiesel has lower emissions of carbon monoxide, particulate matter and unburned hydrocarbons.

Biodiesel has been further converted into emulsified biodiesel (E-biodiesel). It is a proprietary blend of water, a surfactant additive and biodiesel, and has been as substitutes of diesel and biodiesel. According to Lif and Holmberg (2006), E-biodiesel or water-in-oil biodiesel has advantages of reduced emissions of nitrogen oxides and particulate matters; in addition, it reduces fuel consumption with better combustion efficiency. It is incomprehensible as to how biodiesel with water can be used for power generation and this sort of information is often treated as confidential.

Singh *et al.,* (2010) stated that different sources of oil have different fatty acid composition that may vary in the length of carbon chain and the number of unsaturated bonds. Therefore in this study, we attempt to characterise the functional group properties of various fuel sources including biodiesels prepared from various vegetable oils, emulsified biodiesel, petrol and diesel. However, the IR spectra from a variety of feedstocks for biodiesel show very similar profile (Sanford *et al*., 2009).

Objectives

In specific, the objectives of the study are:

1. To prepare the biodiesel from various sources of vegetable oils including corn, canola, palm olein, blend of peanut and sesame and soya oils.
2. To produce emulsified biodiesel for comparisons with the basic biodiesels.
3. To characterise the functional group properties of various biodiesels, emulsified biodiesel, petrol and diesel.

2.0 Literature Review

2.1 Biodiesel

Biodiesel is an alternative source to the widely used petroleum derived diesel fuel. The study on biodiesel has received increasing attention because of its beneficial value to the environment. It can be generated by domestic sources such as soybeans, rapeseeds, coconuts, and even used cooking oil (Balat, 2010).

Biodiesel is biodegradable, non-toxic and environmental friendly (Krawczyk, 1996); in addition, it has low emission profiles and is cheaper than other fuels. Xu (2003) reported biodiesel as a clean renewable fuel and has recently been consider as the best candidate for diesel fuel substitution as it can be used in any compression ignition engines without the need for modification.

Chemically, biodiesel is consisted of monoalkyl esters of long chain fatty acids which can be derived from renewable lipid feedstock such as vegetable oils or animal fat (Xiaoxiang *et al*., 2010). Triacylglycerols or triglycerides (TAG) are the major components of vegetable oils and animal fats (Knothe, 2005). They are esters of fatty acids with glycerol. Upon transesterification in the presence of alcohol, they are converted into biodiesel.

2.1.1 Transesterification of biodiesel

Transesterification is the common way to produce biodiesel. In this reaction, the feedstock (vegetable oil or animal fat) is reacted with alcohol in the presence of a catalyst to produce alkyl esters of the fatty acids (FA) (Knothe, 2005). Usually base catalyst such as sodium hydroxide (NaOH) and methanol are used for the process.

Methanol is used because of its physical and chemical advantages and it is more economic (Dennis *et al.*, 2010). Ma and Hanna (1999) reported that methanol can react with triglycerides quickly and the alkali catalyst is easily dissolved in it.

Figure 1 shows the transesterification reaction of triglyceride. The product of fatty acid methyl esters are obtained from the transesterification of triglyceride with methanol and glycerol as the side products.

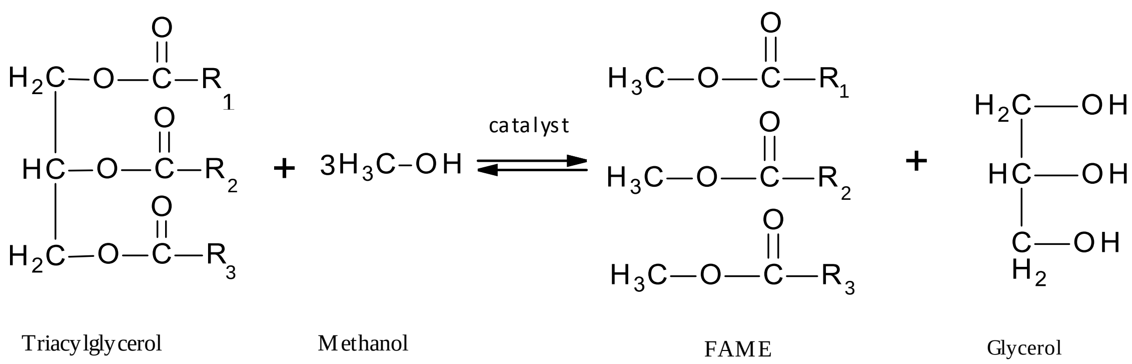

Figure 1: The transesterification process of fatty acid methyl ester (Biodiesel)

Source: Zhang *et al*. (2003)

The transesterification process is by alkali-catalytic reaction. This reaction is performed at a volumetric ratio of oil to methanol of 1:2 with 1% w/v of catalyst (Hossain *et. al.*, 2010). The catalyst is dissolved in methanol by vigorous stirring to form sodium methioxide (Balat, 2010). The catalyst with alcohol mixture is poured into the treated raw oil materials and stirred for an hour. A successful transesterification reaction produces two liquid phases of ester and glycerol, respectively (Demirbas, 2009).

Sodium hydroxide is the most widely used biodiesel catalyst with over 60% of industrial plants using this catalyst (Huber *et al.*, 2006). Singh (2009) revealed that the advantages of using alkaline catalysts are time taken for the reaction is much shorter and a relatively low temperature can be used with only a small amount of catalysts with little or no darkening of the oil. Balat *et al.*, (2010) reported methyl ester of transesterification process has high cetane number, low viscosity and improved heating value that provide shorter ignition delay and longer combustion duration which then results a low particulate emissions.

Drying agent such as magnesium sulphate is used in pre-treatment of the used cooking oil. It is the most efficient for pre-drying according to Lenodard, *et al.*, (1998). Sodium sulphate is used as the drying agent in purification of crude biodiesel after separating biodiesel from glycerol.

2.2 Emulsified biodiesel (E-biodiesel)

The E-biodiesel was evolved by Alternative Petroleum Technologies (APT). It has been known in Europe since the late 1990's (Spataru, 2003). E-biodiesel is the blending of water, a surfactant additive and biodiesel. In the presence of a surfactant additive, two immiscible fluids, oil and water are sheared together and a stable emulsion is produced (Grimes *et al.*, 2011).

Nadem *et al.* (2006) had identified the definition of emulsion as the mixture of two immiscible liquids wherein droplets of one phase (the dispersed or internal phase) are encapsulated within sheets of another phase either in continuous or external phase. Further information from Nadem *et al.* (2006) on forms of emulsion is oil-in-water (O/W) emulsion and water-in-oil (W/O) emulsion. When the oil droplets are encapsulated within the water and dispersed, this situation is called as oil-in-water. Meanwhile, for water-in-oil the water droplets become dispersed and encapsulated within oil.

Blending of all the materials for emulsified fuel will produce white or creamy solution. According to Aponte *et al.* (2012), butter and margarine, milk and cream, espresso and mayonnaise are examples of emulsions. The criteria that is needed for a stable emulsion is the formation of only one phase, but the emulsion will be considered as unstable if more than one layer is observed (Ghannam, 2009).

The unstable emulsions are divided by three types; flocculation, coalescence and cremation; where the particles are concentrated at the surface or bottom which depends on the relative density of the two phases of the mixture while staying separated (Aponte *et al.*, 2012). Sherman (1983) indicates that both processes lead to larger droplets formation until the complete phase of separation occurs.

The presence of water in biodiesel creates micro-explosion phenomenon for the E-biodiesel (Kannan, 2011). Selim and Ghannam (2007) revealed that micro-explosion phenomenon is due to the volatility difference between water and fuel and this enhances air fuel mixing during higher engine torque and hence the improvement in combustion efficiency. This phenomenon also improves the combustion process and reduces hydro-carbon emissions (Kannan, 2011). Ghojel and Honnery (2005) reported that the presence of water in the emulsified fuels has ability to reduce the emission of NO_x.

2.2.1 Surfactant

Surfactant that is often used for blending E-biodiesel is Tween 80, a non-ionic surfactant. Figure 2 shows the chemical structure of Tween 80 or known as polyoxyethylene sorbitan monooleate.

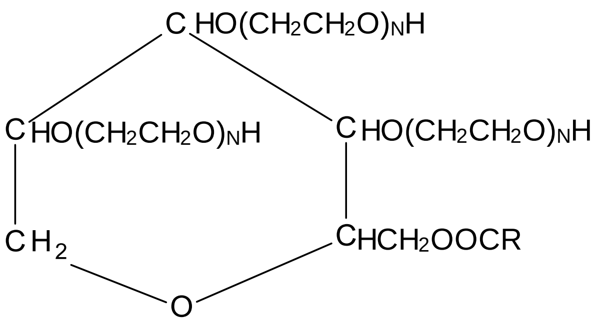

Figure 2: The chemical structure of Tween 80

It is known that oil and water can never work together with well. So, the surfactant is used to help them work together. Selim and Ghannam (2008) stated that surfactant is required to emulsify the fuel and ensure stability for long duration by reducing the interfacial tension. The surfactant works by reduces the surface tension between oil and water, maximizing their superficial contact area, and activating their surfaces.

Cherng and Shiou (2007) stated that the surfactant stabilizes the water and oil due to the hydrophilic and lipophilic groups in the surfactant. The oil phase will absorb by the lipophilic group and the hydrophilic group will absorb the water phase. The emulsifier is one of the examples of the surfactants. This surfactant is burnt readily without soot formation and should not contain sulphur and nitrogen (Lif, 2006). Lif and Holmberg also stated that the surfactants should contain only carbon, hydrogen and oxygen and they should preferably not have aromatic rings in their structure.

2.3 Petrol and diesel

Petrol and diesel are fuels for vehicles derived from petroleum. Singh *et al.* (2010) stated that the average chemical formula for diesel fuel is $C_{12}H_{23}$. Petrol consists of hydrocarbons between five and twelve carbon atom per molecule. Both of products are obtained from fractions of crude oil at different boiling point range.

The chemical structure of diesel fuel contains only carbon and hydrogen atoms that are arranged in straight chain or branched chain structures, as well as aromatic configuration (Singh *et al.*, 2010). Kapur *et al.* reported that the normal structures are preferred for better ignition quality.

Petrol is a mixture of hydrocarbons such as alkanes, aromatic compound and alkene (Bawase *et al.*, 2012). These two types of commercial fuels are for internal combustion engines for motor vehicles. A complete combustion of petrol produces mainly carbon dioxide and water (Pedersen *et al.*, 2003). As in Lin and Pan (2011) research, carbon dioxide is one of the pollutants that will cause serious pollution to the environment such as the green house effect and global warming.

The quality of fuel is determined based on their composition and types of hydrocarbons present in the mixture (Albahri *et al.*, 2002). The quality of petrol is indicated by the octane number (Pedersen *et al.*, 2003).

3.0 Materials and methods.

3.1 Materials

Cooking oil of various origins including corn oil, palm olein oil, canola oil and soya oils are used to produce biodiesel. Other materials required for drying and production of E-biodiesel are magnesium sulphate, $MgSO_4$, sodium sulphate, Na_2SO_4, methanol, sodium hydroxide (NaOH), water and surfactant (Tween 80). The petroleum based products used for comparisons are Petrol RON 95 and diesel.

3.2 Methods

3.2.1 Pre-treatment of the cooking oil

The cooking oil was filtered and added with the drying agent ($MgSO_4$). The oil sample was then stirred for 30 minutes at the room temperature and filtered.

3.2.2 Transesterification of variety types of feedstock oil

Different types of feedstock were poured into the beakers. Sodium methoxide was formed by dissolving 1g of NaOH in 45 ml of methanol. The sodium methoxide was then poured into the oil. This mixture was stirred for an hour at the room temperature. In this process, the oils were subjected to methyl esters conversion using sodium methoxide. After one hour, this mixture was left to separate in the funnel.

3.2.3 Purification of crude biodiesel

At the end of transesterification, two layers of biodiesel and glycerol was formed as illustrated in Figure 3. The bottom layer is glycerol and the top is the biodiesel. The biodiesel was separated from glycerol and drying agent (Na_2SO_4) was added to the biodiesel. The mixture was stirred continuously and filtered yielding biodiesel as shown in Figure 4.

Figure 3: Layers of glycerol and biodiesel

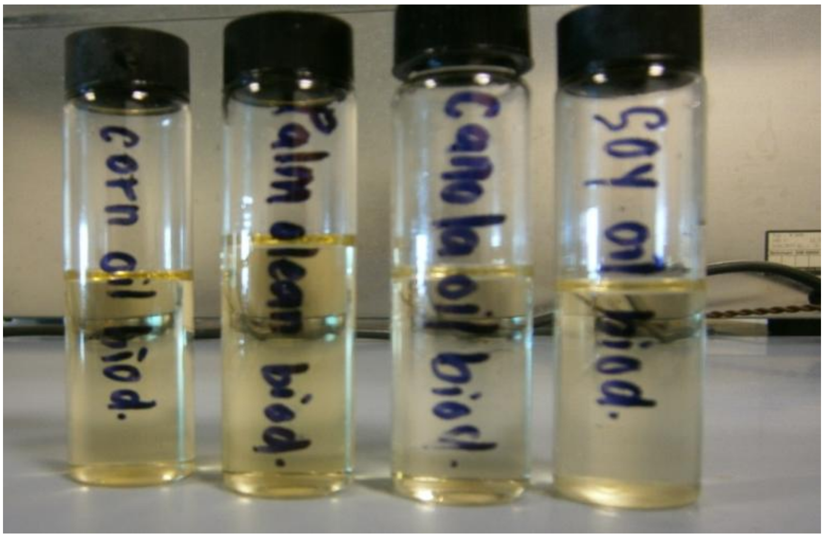

Figure 4: The biodiesel

3.2.4 Functional characterisation by using FTIR.

The different types of biodiesel, petrol and diesel were examined using ATR-FTIR (Attenuated total reflectance-FTIR, Thermo Scientific). A drop of liquid sample was placed onto the ZnSe crystal. The sample was scanned between 4000 cm^{-1} to 650 cm^{-1} in triplicates.

3.2.5 Preparation of E-biodiesel.

The biodiesel was mixed with 5% of water and 2% of surfactant and homogenised. First, the biodiesel was heated around 40-50 ^oC, whilst the surfactant was mixed with water. The mixture was homogenised on a vortex. After that, the mixture of surfactant and water was poured into the biodiesel and blended on the homogenizer. A white and creamy emulsion was produced after the blending of all the materials.

4.0 Results and discussions

4.1 Biodiesel

4.1.1 IR spectra of biodiesel

Figure 5 shows the IR spectra of biodiesels produced from different types of vegetables oil. Biodiesel is primarily comprised of mono-alkyl esters of fatty acids. This is confirmed by the presence of an intense band of C=O stretching of methyl ester and $O\text{-}CH_3$ group. It is important to identify the absorption band attributed to $O\text{-}CH_3$ group because this band confirms that the transesterification process has taken place (Darwin Sebayang *et al.*, 2010).

Basically, the FTIR profile of biodiesel from different feedstock is similar with several major absorption bands at 1740 cm^{-1}, 1196 cm^{-1}, 2922 cm^{-1} and 1460 cm^{-1}. Sanford *et al.* (2009) likewise revealed that biodiesels produced from various feedstocks are similar. This is proven by the absorption spectra in the figure 5 that shows similar transmittance pattern within the range 3000 cm^{-1} to 500 cm^{-1}. The functional groups designated to the major absorption bands are summarised in Table 1. Figure 5 shows the spectra of biodiesels from various origins.

Table 1: Major bands of FTIR spectra of biodiesel

Wavenumber (cm-1)	Functional groups
1740	C=O group
1196	$CH_3\text{-}O$
2922 & 2852	C-H stretch
1460	CH_2 bend
1433 - 1436	$-CH_3$ asymmetric
1168 - 1170	$C\text{-}CH_2\text{-}O$ vibration

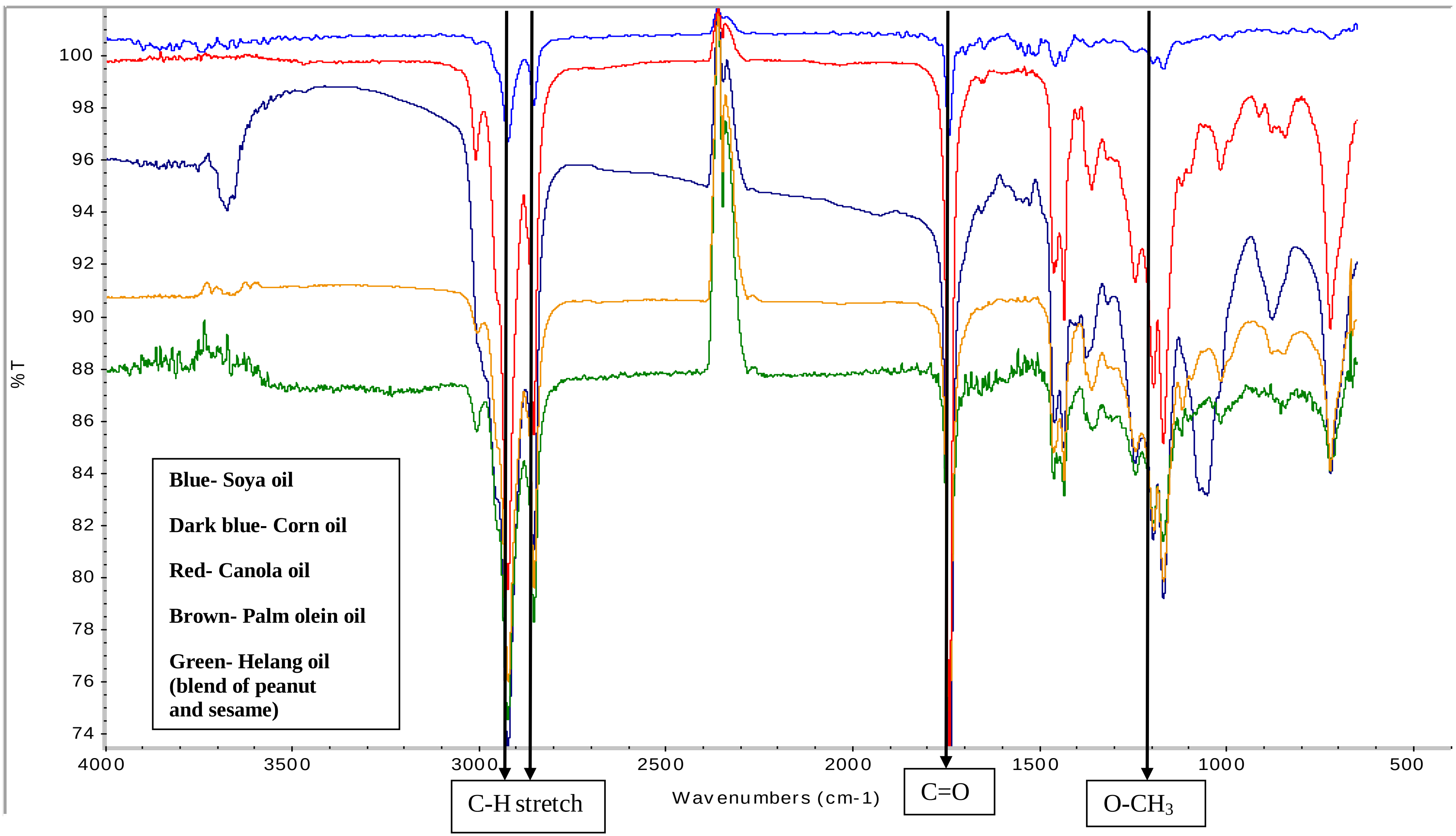

Figure 5: IR spectra of different biodiesels from various origins

The transmittance bands at 2922 cm^{-1} and 2852 cm^{-1} shows the presence of aliphatic hydrogen (Xiaoxiang, Ellis, & Zhaoping, 2011). In region from 4000 cm^{-1} to 3400 cm^{-1} shows the difference where the O-H stretching shows different absorption spectra. Apart from that, 1700 cm^{-1} to 1800 cm^{-1} shows the biodiesel presents a prominent peak that corresponds to the carbonyl group (C=O) (Adriano *et al*., 2007) with soya oil based biodiesel demonstrate relatively weaker absorption. According to Sharma *et al*. (2008), the greater the free fatty acid contains has less possibility the conversion of fatty acid methyl ester. So, the presence of prominent peak for soya oil biodiesel shows weak transmittance absorption.

4.2 Diesel and petrol

4.2.1 IR spectra of diesel

Diesel is one of the commercial fuels that is widely used in our daily lives. According to Singh *et al.* (2010) the chemical structure of diesel fuel contains carbon and hydrogen atoms that are arranged in straight chain or branched chain structures, as well as aromatic configuration. The absorption band at 2924 cm^{-1} and 2854 cm^{-1} shows the C-H stretching vibration. The characteristics peak at 2955 cm^{-1} shows the presence of CH_3. Apart from that, the peak at 1605 cm^{-1} shows the aromatic C-C stretching and the band at 1463 cm^{-1} shows aromatic C=C stretching. At 741 cm^{-1}, the absorption band indicates C-H stretching (out of plane) suggesting the presence of mono substitute. Figure 6 shows the IR spectrum of diesel.