

# Review

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### **Biodiesel Production from Waste Cooking Oil**

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THE INCREASING awareness of the depletion of fossil fuel resources and the environmental benefits of biodiesel fuel has made it more attractive in recent times. The cost of biodiesel, however, is the major hurdle to its commercialization in comparison to petroleum-based diesel fuel. The high cost is primarily due to the raw material, mostly neat vegetable oil. Used cooking oil is one of the economical sources for biodiesel production. However, the products formed during frying, can affect the transesterification reaction and the biodiesel properties. This review attempts to review various technological methods of biodiesel production from used cooking oil. The analytical methods for high quality biodiesel fuel from used cooking oil like GC, HPLC and TGA have also been used. In addition, the specifications provided by different countries are presented. The fuel properties of biodiesel fuel from used cooking oil were also reviewed and compared with those of conventional diesel fuel.

**Keywords:** Biodiesel, Environmental, Diesel fuel and Catalysis.

Energy use is the most fundamental requirement for human existence. It is indeed the livewire of industrial, food and agricultural production, the fuel for transportation as well as for the generation of electricity in conventional thermal power plants. A high percentage of the world's total energy output is generated from fossil fuels and it is has been universally conceded that fossil fuels are finite. The world is no longer endowed with new sources of cheap fossil fuels and experts have warned about the depletion of the present sources in the near future. Furthermore, the threat of supply instabilities and the increased public awareness on the impacts of fossil fuel emissions on the environment and their potential health hazards triggered governments around the world to impose restrictions on fossil fuel combustion emissions<sup>(1)</sup>.

These have simulated interest in alternative sources for fossil fuels especially petroleum-based. One of the most promising sources is biomass<sup>(2,3)</sup>. Among the biomass sources, vegetable oils and animal fats have attracted much attention as a potential resource for production of an alternative for petroleum-based diesel fuel. This alternative diesel fuel is termed biodiesel. This fuel is biodegradable and non-toxic and has low emission profiles as compared to petroleum diesel<sup>(4)</sup>. A major criticism often leveled against bio-fuels, particularly against large-scale

fuel production, is that it could divert agricultural production away from crops, especially in developing countries<sup>(5)</sup>. The basic argument is that energy-crop programs compete with food crops in a number of ways and thus could cause food shortages and price increase. This criticism was re-enacted recently following the rise in cost of food items around the world. As a result of this and the potential benefit in the reduction of liquid waste and the subsequent burden of sewage treatment, this review concentrates on the review of various methods of production of biodiesel from used cooking oils (UCOs). Vegetable oils as engine fuels during the World Exhibition in Paris in 1900, Rudolf Diesel tested vegetable oil for his compression ignition engine<sup>(6)</sup>. However, with the advent of cheap petroleum, appropriate crude fractions were refined to serve as fuel and diesel fuels and diesel engines evolved together<sup>(7)</sup>. In the 1930s and 1940s, vegetable oils were used as diesel substitutes from time to time, but usually only in emergency situations. Recently, because of increases in the price of crude oil, limited resources of fossil oil and environmental concerns, there has been a renewed focus on vegetable oils and animal fats to make biodiesel. Vegetable oils occupy a prominent position in the development of alternative fuels although, there have been many problems associated with using it directly in diesel engines especially in direct injection engine<sup>(4,7-9)</sup>. These problems are associated with large triglyceride molecule and its higher molecular mass can be solved, if the vegetable oils are chemically modified to biodiesel, which is similar in characteristics to diesel<sup>(9,10)</sup>.

The use of biofuels as an alternative source of transportation energy is promoted via national and international legislation and protective measures, as their production enhances sustainability and economic growth. Biodiesel is the most common biofuel employed in Europe and its production (mostly via transesterification) is mainly based on raw vegetable oil<sup>(11)</sup>. Vegetable oil is produced from oil based crops (rapeseed, soy-bean, palm, sunflower ..., etc.) which gives moderate yields per hectare. Besides the importance of producing and using biofuels, there are several considerations associated with the existing production processes. The price and availability of the main byproduct glycerin are both an economic but also environmental consideration.

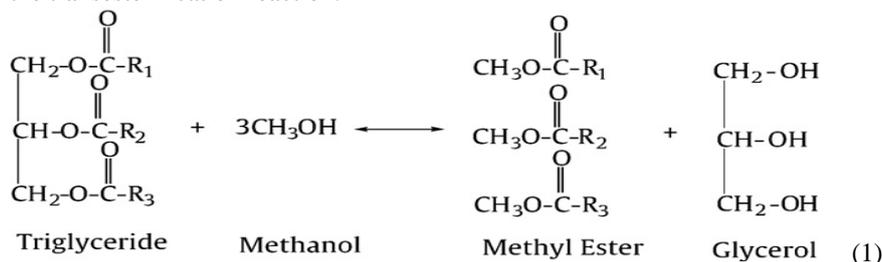
At the present there is no systematic method of processing used oils from households and most of the used oil is mostly thrown through the home drains and ends up in wastewaters that are then discharged to surface waters, leading to water pollution. Moreover, more than 80% of the oil is consumed at home; the control of this disposal behavior becomes a huge problem because of the large volumes involved<sup>(12)</sup>.

Despite the gains made in biodiesel production techniques, the cost of biodiesel is still higher than petroleum-based diesel and this has been a major barrier to its commercialization. One of the ways widely accepted for reducing the cost focuses on minimizing the raw material cost. The use of waste cooking oil instead of virgin (neat) oil to produce biodiesel has been found to be an effective way to reduce the raw material cost. Hence reusing of the waste cooking oil has both the benefit of producing an environmentally benign fuel and solving the problem of waste oil disposal<sup>(13)</sup>.

Furthermore, existing technologies demand large biodiesel production units which require large investments<sup>(14)</sup>. However the most important consideration is the price and availability of vegetable, oil, the cost of which might reach up to 75% of the total production cost<sup>(15)</sup>. The latter can be compensated by employing used cooking oil collected from restaurants and/or homes, the price of which is at least 2–3 times cheaper than virgin vegetable oils<sup>(16)</sup>. Used cooking oil has been explored as a feedstock for biodiesel production via transesterification techniques. Alkali-catalyzed transesterification of a single step<sup>(15,17)</sup> or of a two steps process<sup>(18,19)</sup> gives high yields at moderate methanol/oil ratios and mild temperatures. Another interesting technology is based on heterogeneous solid catalyst-based transesterification<sup>(20-22)</sup> which employs more environmentally benign catalysts and is effective for used cooking oil feedstocks, but requires higher temperatures. Enzymatic- catalysis-based transesterification exhibits significant yields at moderate operating conditions<sup>(23-26)</sup> and shows significant potential. Additionally, catalytic hydrocracking is an alternative technology for biofuels of used cooking oil which studied as a potential process for biofuels production.

### Biodiesel

Biodiesel is an alternative diesel fuel derived from vegetable oils or animal fats<sup>(27)</sup>. The main components of vegetable oils and animal fats are triglycerides or also known as esters of fatty acids attached to a glycerol. Normally, triglycerides of vegetable oils and animals fats consist of several different fatty acids. Different fatty acids have different physical and chemical properties and the composition of these fatty acids will be the most important parameters influencing the corresponding properties of a vegetable oils and animal fats<sup>(28)</sup>. Direct use of vegetable oils and animal fats as combustible fuel is not suitable due to their high kinematic viscosity and low volatility. Furthermore, its long term use posed serious problems such as deposition, ring sticking and injector chocking in engine<sup>(29)</sup>. Therefore, vegetable oils and animal fats must be subjected to chemical reaction such as transesterification to reduce the viscosity of oils. In that reaction, triglycerides are converted into fatty acid methyl ester (FAME), in the presence of short chain alcohol, such as methanol or ethanol, and a catalyst, such as alkali or acid, with glycerol as a byproduct<sup>(27)</sup> Eq. (1) depicts the transesterification reaction.



*Composition of vegetable oils and fats*

Vegetable oils and animal fats usually have hydrophobic properties, which mean they are insoluble in water. As mentioned earlier, triglycerides are made up of 1 mol glycerol and 3 mol fatty acids. Fatty acids vary in terms of carbon chain length and number of unsaturated bonds (double bonds). Typical fatty acids compositions found in several vegetable oils are summarized in Table 1<sup>(30)</sup>. Fatty acids that have no double bonds are termed “saturated” such as stearic acid. These chains contain maximum number of possible hydrogen atoms per atom carbon. Fatty acids that have double bonds are termed “unsaturated” such as Linoleic acid. These chains do not contain maximum number of hydrogen atoms due to the presence of double bond(s) on some carbon atoms<sup>(31)</sup>.

**TABLE 1. Typical fatty acid composition for different common oil source<sup>(31)</sup>.**

Fatty Acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric (C12:0)	0.1	0.1	0.1	0.1	0.1	46.5
Myristic (C14:0)	0.1	0.7	1.0	1.4	0.8	19.2
Palmitic (C16:0)	0.2	20.1	42.8	23.6	23.3	9.8
Stearic (C18:0)	3.7	2.6	4.5	14.2	19.4	3.0
Oleic (C18:1)	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic (C18:2)	53.7	55.2	10.1	10.7	10.7	2.2
Linoleic (C18:2)	8.6	0.6	0.2	0.4	0.4	0.0

*Composition of biodiesel*

Biodiesel is a mixture of fatty acid alkyl esters. In the case when methanol is used as reactant, it will be a mixture of fatty acid methyl esters (FAME) whereas if ethanol is used as reactant, the mixture will be fatty acid ethyl esters (FAEE). However, methanol is commonly and widely used in biodiesel production due to their low cost and availability. Based on different feedstock, the biodiesel produced will have different composition of FAME. Table 2 shows the common composition of FAME in biodiesel<sup>(30)</sup>.

**TABLE 2. Chemical structures of common FAME (fatty acid methyl esters)<sup>(31)</sup>.**

Methyl ester	Formula	Common acronym	Molecular weight
Methyl palmitic	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	C16:0	270.46
Methyl stearate	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	C18:0	298.51
Methyl oleate	C <sub>19</sub> H <sub>36</sub> O <sub>2</sub>	C18:1	296.50
Methyl linolenate	C <sub>19</sub> H <sub>34</sub> O <sub>2</sub>	C18:2	294.48
Methyl linolenate	C <sub>19</sub> H <sub>24</sub> O <sub>2</sub>	C18:2	292.46

### *Catalyst and alcohol*

In general, there are three categories of catalysts used for biodiesel production: alkalis, acids, and enzymes<sup>(32-34)</sup>. Enzyme catalysts have become more attractive recently since they can avoid soap formation and the purification process is simple to accomplish. However, they are less often used commercially because of the longer reaction times and higher cost. To reduce the cost, some researchers developed new biocatalysts in the recent years. An example is so called whole cell biocatalysts which are immobilized within biomass support particles. An advantage is that no purification is necessary for using these biocatalysts<sup>(35-38)</sup>. Compared with enzyme catalysts, the alkali and acid catalysts are more commonly used in biodiesel production<sup>(39)</sup>. The alkali and acid catalysts include homogeneous and heterogeneous catalysts. Due to the low cost of raw materials, sodium hydroxide and potassium hydroxide are usually used as alkali homogeneous catalysts and alkali-catalyzed transesterification is most commonly used commercially<sup>(40-47)</sup>. These materials are the most economic because the alkali-catalyzed transesterification process is carried out under a low temperature and pressure environment, and the conversion rate is high with no intermediate steps. However, the alkali homogeneous catalysts are highly hygroscopic and absorb water from air during storage. They also form water when dissolved in the alcohol reactant and affect the yield<sup>(48)</sup>. Therefore, they should be properly handled.

On the other hand, some heterogeneous catalysts are solid and they could be rapidly separated from the product by filtration, which reduces the washing requirement. In addition, solid heterogeneous catalysts can stimulatingly catalyze the transesterification and esterification reaction that can avoid the pre-esterification step, thus these catalysts are particularly useful for those feedstocks with high free fatty acid content<sup>(49)</sup>. However, using a solid catalyst, the reaction proceeds at a slower rate because the reaction mixture constitutes a three-phase system, which, due to diffusion reasons, inhibits the reaction<sup>(50-61)</sup>.

The alcohol materials that can be used in the transesterification process include methanol, ethanol, propanol, butanol, and amyl alcohol. Among these alcohols, methanol and ethanol are used most frequently. Methanol is especially used because of its lower cost and its physical and chemical advantages. Ma and Hanna<sup>(62)</sup> reported that methanol can react with triglycerides quickly and the alkali catalyst is easily dissolved in it. However, due to its low boiling point, there is a large explosion risk associated with methanol vapors which are colorless and odorless. Both methanol and methoxide are extremely hazardous materials that should be handled carefully. It should be ensured that one is not exposed to these chemicals during biodiesel production<sup>(63)</sup>.

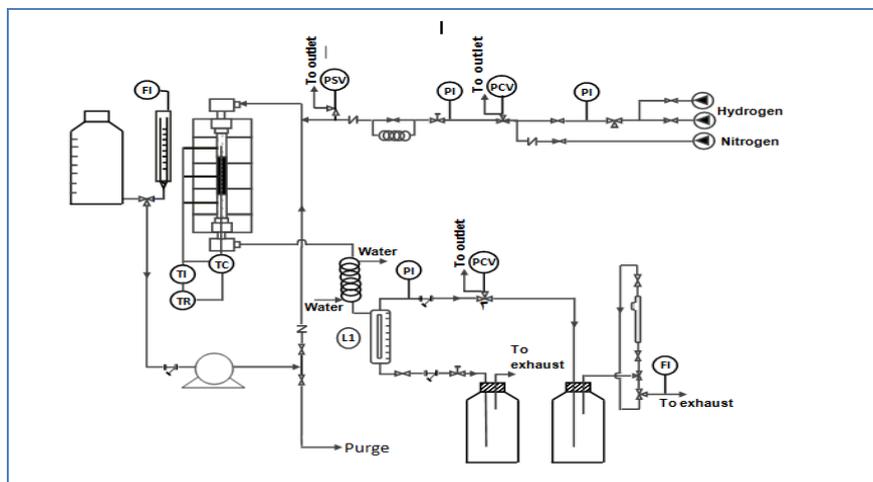
### *Catalytic hydroprocessing*

Catalytic hydroprocessing is an alternative technology for biofuels production technology which employs the existing infrastructure of petroleum refineries<sup>(64, 65)</sup>, and has already several<sup>(66,67)</sup>. The technology has significant potential as the produced hydrotreated vegetable oils have better fuel properties than the biodiesel produced via transesterification, and their use improves engine fuel

economy<sup>(64)</sup>. Hydroprocessing of raw vegetable oil + heavy vacuum gas oil mixtures have been explored by employing hydrotreating<sup>(68)</sup> and hydrocracking<sup>(69)</sup> catalysts at nominal operating conditions. Nevertheless, this technology has only been applied to raw vegetable oil feedstocks<sup>(70)</sup>.

This review discusses the investigation of used cooking oil as a hydrocracking feedstock as well as the key parameters affecting product yield and quality of such process. In particular, the effect of reactor temperature and liquid hourly space velocity (LHSV) on product yields and quality are studied. Furthermore, the dependence of the hydrocracking effectiveness on the catalyst life (days on stream) is also explored. It should be mentioned that it is the first application of catalytic hydroprocessing on used cooking oil.

The experimental set up used for testing the catalytic activity is carried out using continuous high pressure unit (cata-test unit) which is employed for hydrotreating (HDS, HDN) and hydrocracking of various feedstocks, varying from light gas oil to heavy vacuum gas oil (Fig. 1). The total liquid product is collected and several analyses can take place. The density of the total liquid product is measured according to ASTM D-1052. The concentration of sulfur and nitrogen is measured according to ASTM D5453-93 and ASTM D4629 procedures, respectively. Total carbon concentration is measured via a CHN LECO 800 analyzer.



**Fig. 1. Continuous high pressure unit (cata-test unit) .**

The catalyst was pre-sulphided according to the catalyst provider's recommended procedure. Furthermore, in order to maintain constant catalyst activity, DMDS (Di-Methyl-Di-Sulfide) and TBA (Tetra-Butyl-Amine) were added to achieve a specific sulfur and nitrogen concentration in each feedstock. An experiment was considered complete when the reactions reached steady state.

Once the product density was stabilized, the individual effects of each experiment were considered stable and the study complete. In order to analyze the effectiveness of hydrocracking reactions, hydrocracking conversion can be employed. Hydrocracking conversion (%) is defined as the percentage of the heavy fraction of feed which has been converted to lighter products during hydrocracking:

$$\text{Conversion \%} = \frac{\text{Feed}_{360} - \text{Product}_{360}}{\text{Feed}_{360}} \times 100 \quad (2)$$

where  $\text{Feed}_{360}$  and  $\text{Product}_{360}$  are the wt% of the feed and product, respectively, which have a boiling point higher than 360 °C. Furthermore, in order to measure the hydrocracking effectiveness towards the production of a particular product instead of other products, the measure of selectivity is employed. Selectivity can be defined for different products (ex diesel, gasoline ..., etc.) based on the boiling point range which defines these products. For example, for a product with initial and final boiling points A and B, respectively, selectivity  $_{A-B}$  is defined as:  $\text{Feed}_{A-B}$

$$\text{Product selectivity \%} = \frac{\text{Product}_{(A-B)} - \text{Feed}_{(A-B)}}{\text{Feed}_{(360\text{oC})} - \text{Product}_{(360\text{oC})}} \times 100 \quad (3)$$

where  $\text{Feed}_{360\text{oC}}$  and  $\text{Product}_{360\text{oC}}$  are the wt% of the feed and product, respectively, which have a boiling point higher than 360°C (*i.e.*, heavy molecules of feed and product) and  $\text{Feed}_{A-B}$  and  $\text{Product}_{A-B}$  are the wt% of the feed and product, respectively, which have a boiling point range between A and B degrees Celsius. From Eq. (2) selectivity can be defined for diesel (180–360 °C), kerosene/jet (170-270 °C) and naphtha (40-200°C).

A series of experiments were conducted to study the effect of reactor temperature and liquid hourly space velocity (LHSV) on hydrocracking of used cooking oil. Moreover, the effects of catalyst deactivation are also explored. The feedstock employed was 100% used cooking oil. The used cooking oil was mainly collected from local restaurants, while smaller amounts (<10 vol %) of domestic used cooking oil were also employed. The used cooking oil was filtered via a regular sieve to remove any food particles remaining in the oil after frying. Typical characteristics of the various sources of used cooking oil are given in Table 3<sup>(70)</sup>.

**TABLE 3. Properties of different sources of used cooking oil.**

	<b>Domestic</b>	<b>Restaurants, taverns</b>	<b>Fast food</b>
Density (kgr/m <sup>3</sup> )	0.8929	0.8993	0.8969
S (wppm)	0.00	187.70	26.30
N (wppm)	0.40	49.10	61.90
H (wt %)	11.56	11.52	11.58
C (wt %)	77.24	76.53	76.32
O (wt %)	11.20	11.92	12.09
Refractive index	1.45602	1.45561	1.45463
Bromine index	46.6	43.1	44.3

*Effect of reactor temperature*

Temperature has been identified as a key parameter for catalyst effectiveness and catalyst life<sup>(71)</sup>. Increasing temperature increases catalyst activity and increasing catalyst activity causes a faster decay of catalyst life. For this reason the effect of hydrocracking temperature on all reaction types (cracking, saturation and heteroatom removal) is explored. This study on product yields and quality was performed on hydrocracking of used cooking oil at different reactor temperatures.

The diesel yield is estimated as the vol % of the total liquid product that has a boiling range between 180 and 360°C, while the gasoline yield is the vol% of the total liquid product with a boiling range between 40 and 200°C. Lighter products (with boiling point < 40°C) are gaseous molecules and are not considered in this analysis as liquid biofuel product. Moreover, heavier molecules (with boiling point > 360°C) compose the unconverted part of the feed that cannot be utilized as liquid biofuels. The product yields increase as reactor temperature increases, the produced liquid biofuels (gasoline and diesel) increase, this is expected as hydrocracking activity rises with increasing temperature. Diesel yield is more than seven times higher than the gasoline yield at all temperatures, indicating that this technology is more suitable for diesel production rather than gasoline production<sup>(70)</sup>. Furthermore, gasoline yield increases monotonically with temperature, while diesel yield is smaller at the middle temperature (370 °C). The minimum diesel yield observed at 370 °C is attributed to the fact that increasing temperature causes not only heavy molecules but also diesel ones are cracked into lighter molecules<sup>(69)</sup>. The conversion as well as the diesel, kerosene/jet and naphtha selectivities for the different hydrocracking temperatures. The conversion and selectivities are calculated from the simulated distillation data of the total liquid product of each hydrocracking temperature, using Eq. (2) and (3), respectively, as temperature increases, the conversion increases, this is an expected outcome as hydrocracking activity is favoured with temperature<sup>(70)</sup>. Diesel selectivity has the most significant values (>90%), as diesel production is most favorable. In the mean time kerosene/jet and naphtha selectivities are below 20%<sup>(70)</sup>. This is expected as increasing temperature causes more intensive

cracking thus not only heavier molecules but also some diesel molecules are further cracked into lighter molecules. Therefore, milder hydrocracking temperatures (350 and 370°C) promote diesel rather than kerosene/ jet or naphtha production.

According to the hydrogenation effect on the hydrocracked product at the different reactor temperatures, the bromine index (Bromine index indicates the presence of olefins or double bonds) increases for increasing hydrocracking temperature, signifying that the saturation of double bonds decreases as reactor temperature increases. Therefore, catalyst activity is primarily driven towards cracking or other reactions rather than saturation, which indicates that a hydrotreatment step might be necessary prior to hydrocracking. The same conclusion is drawn; the C/H ratio significantly dropped from feed to products, however, it increases as hydrocracking temperature increases. Besides cracking and saturation, heteroatom removal (mainly sulfur, nitrogen and oxygen) is another group of reactions that take place during hydrocracking. Clearly the efficiency of heteroatom removal for all three species (S, N and O) is high and is increasing with hydrocracking temperature<sup>(70)</sup>.

#### *Effect of LHSV*

The Liquid Hourly Space Velocity (LHSV) is an important operating parameter for regulating catalyst effectiveness and also catalyst life expectancy. The effect of LHSV on cracking is the main premise of this analysis. This review on product quality and yields was performed on hydrocracking of used cooking oil at different LHSVs h<sup>-1</sup>. However, an overall decreasing trend is observed with increasing LHSV, which is expected, as increasing LHSV implies smaller residence time of the feed in the catalyst section (reactor) and therefore smaller reaction time. Diesel yield is significantly higher than gasoline yield at all LHSVs. The conversion as well as the diesel, kerosene/jet and naphtha selectivities for the different LHSVs. The conversion decrease for increasing LHSV is anticipated since high LHSVs result in smaller reaction time. Regarding individual product selectivities, on one hand, the diesel selectivity exhibits once again the most significant values. On the other hand, the kerosene/jet and naphtha selectivities are lower value for all LHSVs. Furthermore, diesel selectivity is favoured with LHSV while kerosene/jet and naphtha selectivities are not. This is also expected as increasing LHSV (therefore decreasing reaction time) causes less cracking and therefore a smaller production of the lighter products (kerosene/jet and naphtha). Therefore, higher LHSVs promote diesel than kerosene/jet or naphtha production<sup>(70)</sup>.

#### *Effect of catalyst life (days on stream)*

The industrial hydrocracking unit run length is one of the most crucial parameters of catalyst selection and is mainly limited by catalyst life. Catalyst life or catalyst aging is mostly attributed to extended operation or by blockage of active sites attributed to the feedstock components. As it is extremely important to anticipate typical reasons for deactivation, this review aims to assess this technology during an early stage and a latter stage of the experiment. For this

analysis two experimental runs were employed using the same hydrocracking catalyst. The only difference between the two runs was that data from RUN-A were collected at an early stage of the experimental run while data from RUN-B were collected at a latter stage of the experimental run. Conversion is a key assessment measure of catalyst activity and its stability on increasing operation time indicates good catalyst life expectancy. Increasing operation time in pilot plant experimental protocols is expressed as increasing number of days that feedstock is flowing over the catalyst, *i.e.* days on stream or DOS. For RUN-A conversion gradually increases with temperature as expected, since increasing temperature favors cracking. However, conversion exhibits a different behaviour at higher DOS. Therefore, after extended day DOS the catalyst activity is decreased and increasing temperature is not able to compensate for this activity loss, possibly due to catalyst blockage by the large feed molecules<sup>(70)</sup>.

The hydrogenation effectiveness at increasing DOS is examined, in particular for both runs C/H ratio % of C/H of feed is monotonically decreasing with increasing temperature as it was discussed above, since saturation is not favored with temperature. However in the case of higher DOS (RUN-B) this C/H ratio decrease, indicating that after extended day DOS the ability of the catalyst to allow saturation is hydrant. Therefore, the extended DOS cause an increasing inhibition of saturation activity.

Finally the heteroatom removal effectiveness for extended DOS, where the removal of all atoms (S, N and O) is decreasing for increasing DOS but the effect of DOS is different for all atoms.

In the case of sulfur and nitrogen removal it is clear that after the passage of days the ability of the catalyst to remove these atoms is decreased as the results between RUN-A and RUN-B are different even at the smallest temperature. Specifically in the case of nitrogen removal the difference is significant, indicating that the effectiveness of nitrogen removal is hindered earlier than the one of sulfur removal. However, the effect of catalyst life on the removal of these atoms is constant as the difference between the RUN-A and RUN-B results is relatively constant. Finally, the effect of DOS on de-oxygenation is observed a little later. However, the effect of catalyst life is stronger for oxygen removal as a significant increase of the difference between RUN-A and RUN-B is observed for increasing DOS<sup>(71)</sup>.

### Conclusions

Biodiesel is a renewable and alternative fuel to petroleum-based diesel that is non-toxic, biodegradable and does not contribute net carbon emission to the atmosphere. Currently, biodiesel is produced through transesterification reaction from vegetable oils such as rapeseed, soybean and palm oil. However, the high prices of these oils in the global market have sharply increased the overall biodiesel production cost making it not economically viable as compared to petrol based diesel. Furthermore, the oils are important commodities in the

human food supply chain and therefore its conversion to biodiesel in a long run may not be sustainable. As an alternative, this review has addressed the potential of using waste cooking oil, as a cheap and economical feedstock for biodiesel production. Nevertheless, current commercial technology (homogeneous base catalyst) was found not suitable for the transesterification of waste cooking oil due to its high FFA content. On the other hand, using homogeneous acid catalyst requires longer reaction time and could potentially cause corrosion on equipment. Therefore, it is clear that research on heterogeneous catalyst, either base or acid type, should be carried out extensively to develop a suitable catalyst to convert waste cooking oil to biodiesel with special emphasis on catalyst deactivation and regeneration.

Hydrocracking of used cooking oil is a prominent process for the production of biofuels. This work considers several parameters for evaluating the effectiveness of this technology, mainly hydrocracking temperature, liquid hourly space velocity (LHSV) and days on stream (DOS). Conversion and overall biofuels' yield is favored with increasing temperature and decreasing LHSV, as cracking activity is increased. However, moderate reaction temperatures and LHSVs are more attractive if diesel production is targeted, whereas higher temperatures and smaller LHSVs should be employed if gasoline production is also important. Heteroatom (sulfur, nitrogen and oxygen) removal is also increasing as hydrocracking temperature increases, with de-oxygenation particularly favorable. Saturation however is not favored with temperature indicating a necessity of a pre-treatment step prior to hydrocracking, to enable saturation of the double bonds prior to cracking and heteroatom removal. Finally, catalyst deactivation was observed by monitoring conversion, heteroatom removal and saturation effectiveness with increasing DOS. In all cases catalyst effectiveness was decreased with increasing DOS but at different rates. Sulfur and nitrogen removal are affected earlier than all other reactions. Saturation reactions are affected only after the maximum DOS studied. Conversion and oxygen removal are also significantly affected and their loss of effectiveness appears more rapid than the other reaction mechanisms.

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## الانتاج الحيوى لزيوت الديزل من بقايا زيوت الطهى

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قسم تكرير البترول – المعهد المصرى لبحوث البترول – القاهرة – مصر.

نظرا للتناقض الذى يدعو إلى القلق فى مخزون وقود الحفريات فإن الأهمية البيئية للإنتاج الحيوى لزيوت الديزل تزداد برغم من الصعوبة فى تسويقه بالمقارنة إلى زيت الديزل المستخرج من البترول ويرجع ارتفاع تكاليف الإنتاج الحيوى لزيوت الديزل إلى ارتفاع سعر المواد الخام وهى أساسا من الزيوت النباتية النقية ولذلك يعتبر استخدام بقايا زيوت الطهى فى الإنتاج الحيوى لزيوت الديزل ملائم جدا من الناحية الاقتصادية ويلقى هذا المقال المرجعى مزيدا من الضوء على مختلف التكنولوجيات المتبعة فى الإنتاج الحيوى لزيوت الديزل من بقايا زيوت طهى الطعام وكذا عرض مختلف الأساليب التحليلية المتبعة للحصول على أنقى صور زيت الديزل و مواصفاته القياسية المتعارف عليها والمقررة فى العديد من بلدان العالم.