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# Upgrading of waste oils into transportation fuels using hydrotreating technologies

Sudipta De [1], Rafael Luque [2]*

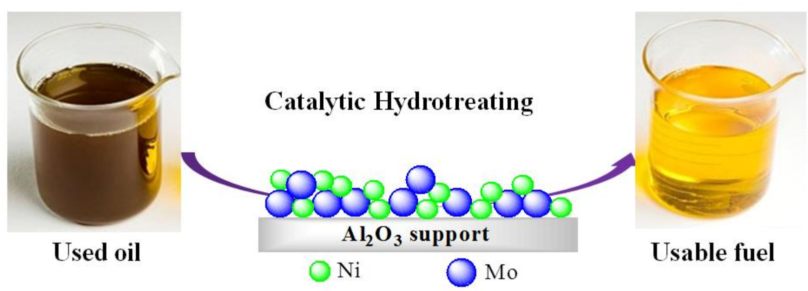
*[1]Laboratory of Catalysis, Department of Chemistry, University of Delhi, North Campus, Delhi-110007, India.*

*[2]Departamento de Quimica Organica, Universidad de Cordoba, Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV-A, Km 396, 14014 Cordoba, Spain.*

## HIGHLIGHTS

- Proper utilization of waste oils to generate transportation fuels using green technologies.
- Catalytic hydrotreating as the most effective technology for waste oil upgrading.
- Selection of low-cost efficient catalysts for hydrotreating process.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The generation of organic waste continues to increase, causing severe environmental pollution. Waste valorization is currently an emerging technology that can address this problem with an extra benefit of producing a range of valued products. In this contribution, we report the current developments in hydrotreating technologies for upgrading waste oil fractions into usable transportation fuels. Particular focus is given on the catalysts selection for a general hydroprocessing technique as well as the competitive role of those catalysts in hydrotreating and hydrocracking processes.



Limited resources along with the negative environmental impact of fossil fuels have urged the society to search for renewable transportation biofuels. Today, more than 35 countries, including the United States, Brazil and members of the European Union, have established several policies to promote the production and use of biofuels (OECD-FAO Agricultural Outlook, 2011). But, the current technologies for the production of biofuels are solely dependent on the food crops. Therefore, the question has been raised whether is it really possible to obtain the required amount of biofuels from renewable resources without threatening food production. Waste valorization is the most sustainable way and a viable alternative that can address the problem. In this consequence, non-edible or used oils are the most suitable renewable feedstocks that can be upgraded into useful diesel range transportation fuels *via* different modern techniques.

Waste oils are one of the most abundant pollutant residues that are

* Corresponding author at: Tel.: +34 957 211 050
E-mail address: q62alsor@uco.es

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generated nowadays. Municipal and industrial wastes contain high heat values in the form of waste oils such as waste plastics oil (WPO), waste cooking oil (WCO), and waste lubricating oil (WLO) that can be considered as efficient feedstocks for energy production in a Waste-to-Energy regimen. Annual global consumption of lubricating oil was estimated at 42 million tons in 2010 and is expected to reach about 45 million tons per year by 2015. These waste oils pose an environmental hazard due to both their metal content and other contaminants (such as high sulfur content). WCOs are the second most abundant waste residue which is generated in enormous amount by restaurants, food processing industries and fast food shops everyday. The worldwide demand for edible vegetable oil keeps growing. In China, with an annual consumption of edible oils approaching 22 million tons, the country generates more than 4.5 million tons of used oil and grease each year (Xiangmei et al., 2008). WCOs are highly viscous and generally contain high oxygen content which is not compatible with the design of motor engines. So, prior to use in engines, these oils are required to be converted into suitable fuels by some advanced processes that can lower their viscosity and oxygen content, and improve their atomization and lubricity (Freedman and Bagby, 1989).

During frying, vegetable oil undergoes various physical and chemical changes, and many undesirable compounds including free fatty acid and some polymerized triglycerides are formed which increase the molecular mass and reduce the volatility of the oil. WCO is rather safer than waste engine oil as it is renewable and does not contain any aromatics, metal or sulfur contaminants. The properties of the oil derived from waste plastics, cooking and engines oils were analyzed and found that it has properties similar to those of diesel. The performance of those waste oil-derived fuels has already been tested in diesel engines with a great success (Naima and Liazid, 2013). Table 1 shows a comparison of fuel properties for a WCO biodiesel and diesel fuel. Besides, WCO has significant sustainability potential as a residual biomass that does not compete with food production, while its reuse can impede environmental problems raised from their disposal as well. Currently, the major barrier for biodiesel commercialization is its high cost, compared to petroleum-based diesel. Approximately 70–85% of the total biodiesel production cost arises from the cost of raw material. Therefore, it is expected that the use of WCO as a low-cost feedstock for biodiesel production could greatly reduce the production cost as it is available at a significantly low price. However, for both cases, improved refining and treating processes are required to convert the high-volume waste oils into valuable fuel products. The process involves conversion of fatty acids in triglycerides into normal and/or iso-alkanes which can be obtained by hydrodeoxygenation, decarbonylation, decarboxylation, isomerisation and hydrocracking or a combination of two or more thereof.

**Table1.**
Comparison of fuel properties for a WCO and diesel fuel (Enweremadu and Rutto, 2010).

| Properties | Waste cooking oil | Diesel |
|---|---|---|
| Density at 15 °C (kg/m$^3$) | 876.08 | 807.3 |
| Specific gravity at 15.5 °C | 0.893 | 0.825 |
| Flash point (°C) | 160 | 53 |
| Fire point (°C) | 164 | 58 |
| Viscosity at 40 °C (mm$^2$/s) | 3.658 | 1.81 |
| Calorific value (kJ/kg) | 39767 | 42348 |
| API gravity | 26.87 | 39.51 |
| Cetane index | 50.54 | 46.21 |

Hydrotreating is one of the most important techniques in the petroleum refinery to remove S, N and metals from petroleum-derived feedstocks including heavy gas-oil or vacuum gas-oil (Farrauto and Bartholomew, 1997). Though the catalytic hydrotreating is a well-known and effective technology with various applications in the petrochemical industry, but only lately it has expanded in the area of bio-oil upgrading. The main advantage of hydrotreating process is that the required infrastructure is widely available in all refinery units. The process leads to a deoxygenated product with a high cetane number and low sulfur content which is fully compatible with the petroleum-derived diesel fuels. Hydrotreating is more advantageous over transesterification because of its lower processing cost, compatibility with infrastructure, NOx emission reduction, and feedstock flexibility.

For any industrial production processes, hydrotreatment consists of two main steps. In the first step, triglycerides of the lipid feedstock are converted into an oxygen-free hydrocarbon-based fuel consisting of primarily normal paraffins. Though the cetane number is improved in this step, the fuels have high cold flow properties which are not suitable enough for an engine use. Therefore, a second hydroprocessing step is needed where isomerization/dewaxing enables the conversion of normal paraffins into iso- and cyclo-paraffins, leading to an improved fuel with sufficiently low cold flow properties. However, the major research should be focused on the first step, the catalytic hydrotreatment for oxygen removal, and therefore, selection of effective catalysts should be taken into consideration.

The selection of a hydrotreating catalyst is a critical step defining the yields and corresponding quality of hydrotreating products. In general, hydrotreating catalysts consist of critical metals such as Mo, Co, and Ni, as active metals and are usually supported by alumina or silica alumina (Bezergianni et al., 2014; No, 2014). Furthermore, the hydrotreatment of waste bio-oils is much more complex than that of petroleum-based feeds. In a petroleum refinery, the major concern of the catalytic process is focused on its hydrodesulfurization (HDS) efficiency. But, for waste bio-oil upgrading, hydrodeoxygenation (HDO) is the major concern along with HDS and therefore, the catalyst selection is of outmost importance. Interestingly, in both processes, hydrogen is used to remove the heteroatom in the form of $H_2O$ and $H_2S$, respectively. Therefore, it is an advantage that several works on bio-oil HDO can use catalytic systems that are already used in HDS processes, such as Co-Mo or Ni-Mo based catalysts.

During hydroprocessing, two probable processes, hydrotreating and hydrocracking may occur simultaneously. In order to obtain diesel range fuel, hydrotreating process is favored which removes hetero atoms and saturate C–C bonds with the number of carbon atoms intact. On the other hand, hydrocraking (severe form of hydroprocessing) favors breakage of C–C bonds, drastically lowering the molecular weight to generate gasoline range fuels. Therefore, if the purpose is to get diesel fuels, then catalysts and reaction conditions should be properly selected that would result in hydrotreating of the feeds with minimal hydrocracking. For example, a combined sulfided Ni–Mo/$Al_2O_3$ catalyst offers a high selectivity for diesel range ($C_{15}$–$C_{18}$) product from a mixture of waste soya oil and gas-oil due to minimal cracking, while a sulfided Ni–W/$SiO_2$–$Al_2O_3$ catalyst gives considerable jet range product due to cracking (Rana et al., 2013). It seems that the hydrodeoxygenation for oxygen removal from triglyceride is favored over the Ni–Mo catalyst, while decarboxylation and decarbonylation are favored over the more acidic Ni–W catalyst. The effect of acidity of the catalyst support is even more prominent when two different supports (e.g., $SiO_2$ and HY zeolite) are used keeping the active metal site intact. Treatment of WCO with a Ru/$SiO_2$ catalyst predominantly produces $C_{15}$–$C_{18}$ (98.9 wt%) liquid hydrocarbon products (Liu et al., 2012). On the other hand, Ru/HY catalyst formed a large amount of $C_5$–$C_{10}$ gasoline-ranged paraffins on the strong acid sites of HY. However, it is observed that the fluidity of the liquid hydrocarbon product over Ru/$SiO_2$ is poor because of a predominant amount of $C_{15}$–$C_{18}$ *n*-paraffins. This can be improved by a multifunctional catalyst support, such as $Al_{13}$-Mont, that can simultaneously facilitate hydrogenation, deoxidization, and isomerization/cracking for the hydrotreatment of WCO, producing similar hydrocarbon products to those of a commercial normal diesel in terms of chemical composition and the pour point.

Considering the production cost, hydrotreating process consumes much more hydrogen and is thus more expensive as compared to hydrocracking. Reducing the volume of hydrogen consumed in the process would make the process economics more favorable. The investment cost of a standalone hydroprocessing unit for vegetable or waste oils is very high. Therefore, it is supposed that the co-processing of petroleum-derived raw materials along with the waste oil could be a solution for the industrial scale production of renewable diesel fuels. NiMo-based catalysts have been explored for co-processing studies that can target both hydrotreating and hydrocracking reactions as discussed earlier. It was also proved that the oxygen removal and desulphurization reactions take place on the same active centers of the catalyst (Toth et al., 2011). The efficiency of the catalysts has been already tested for the catalytic co-processing of vegetable oil–gas oil mixture, in which the product selectivity can be easily tuned by choosing the catalyst. Depending on the acidity of the catalyst support, different catalyst gives different fuel components ranging from kerosene to diesel.

Another major concern is the use of lower quality feedstocks, such as restaurant trap grease which are very difficult to convert by catalytic hydrotreating, due to their heterogeneous nature and the presence of contaminants. These contaminants can rapidly deactivate the catalyst, requiring large quantities of catalyst to be used that increases the operating costs. Therefore, it is an urgent need to find out efficient methods consisting of highly resistant catalysts for the production of a high cetane value product from low quality waste triglyceride feedstocks that can be used as a diesel fuel or as diesel fuel blending stock. Along with this, we need to find out the protocols that will reduce the hydrogen consumption in the catalytic hydrotreating stage. Till date, only few studies have been reported on the hydrotreating technologies in waste oil upgrading and more work needs to be done. Much more positive input is to be given to improve the innovative and emerging green technologies that can lead the way towards an economical and sustainable society for mankind.

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