Transportation fuels from co-processing of waste vegetable oil and gas oil mixtures

CrossMark

Bharat S. Rana, Rohit Kumar, Rashmi Tiwari, Rakesh Kumar, Rakesh K. Joshi, Madhukar O. Garg, Anil K. Sinha*

CSIR-Indian Institute of Petroleum, Mohkampur, Dehradun 248005, India

ABSTRACT

Hydroprocessing catalysts, sulfided Ni–W (on mesoporous silica–alumina) and Ni–Mo (on mesoporous γ-alumina), under typical hydroprocessing conditions, can very effectively produce liquid fuel from mixtures of waste vegetable oil and refinery gas oil. The acidity of the catalyst controls the relative amount of diesel range (straight chain) alkanes and cracked lighter products. The yield of diesel range (250–380 °C) product varied between 60 and 90%, while kerosene (jet) range product varied between 10 and 35% depending upon the reaction conditions and type of catalyst used. The hydrodeoxygenation pathway for oxygen removal from triglyceride seems to be favored over the Ni–Mo catalyst, while decarboxylation + decarbonylation pathway is favored over the Ni–W catalyst and the respective pathways becomes more dominant with increasing vegetable-oil content in the feed. Vegetable oil conversion does not adversely influence hydrodesulfurization of gas oil indicating viability of co-processing. The activation energy for overall S-removal is much lower than that for overall O-removal. Density and acidity (TAN) of the products meet the required specification and cetane number is better than that for pure diesel.

1. Introduction

Increased demand for cleaner fuel due to environmental concern and depleting petroleum reserves coupled with deteriorating quality of the crude oil have led to a surge in world-wide quest for renewable and clean fuel sources [1–4]. One of the renewable sources is biofuels from vegetable oils [5], specifically, non-edible and used oils such as waste restaurant oil [6], jatropha oil [7], algae oil [8], etc. Prior to use in engines, these oils originating from vegetables and animals need to be converted into suitable fuels by processes that can lower their viscosity and oxygen content, and improving their atomization and lubricity [9].

Bio-diesel, which is Fatty Acid Methyl Esters (FAME), is produced by transesterification of fatty acids in triglycerides making it suitable as fuel. However, new biodiesel plants require a large capital investment [10,11] and large quantities of byproduct glycerol needs to have suitable market. To use neat bio-diesel requires some modification in engine and additionally it gives poor performance in cold weather and poor emission. An attractive route that offers engine compatibility and feedstock flexibility using the existing petroleum refinery infrastructure, is the conversion of renewable oils into hydrocarbons which have much higher cetane value than conventional diesel fuel. This process involves conversion of fatty acids in triglycerides into normal and/or iso-alkanes. This may be obtained by hydrodeoxygenation, decarbonylation, decarboxylation, isomerisation and hydrocracking or a combination of two or more thereof [6,7,12–23].

Hydroprocessing is used in the petroleum refinery to crack larger molecules and/or to remove S, N and metals from petroleum derived feedstocks such as, gas oil and heavy oil [24]. Hydroprocessing has now become a well reported [6,7,12−23] and an established process [25−28] to produce straight chain alkanes from fatty acid triglycerides of animal fat, tall oil, and other vegetable oils.

A ten month on − road test showed that engine fuel economy was improved by a blend of petrol diesel with hydrotreated tall oil [18]. The advantage of hydrotreating over trans-esterification are compatibility with current refinery infrastructure, engine compatibility and feedstock flexibility [18]. Neste oil corporation and UOP have developed technologies for producing diesel fuel from vegetables oils in refineries using modified hydrotreating process [27,28]. *Glycine max* (Soya), being a food-crop and richest, cheapest and easiest source of best quality proteins and fats and having a vast multiplicity of uses as food and industrial products, cannot be used as fuel feedstock being. Waste vegetable oil such as *G. max* (soya) is produced, mainly from industrial deep fryers, snack food factories, restaurants and hotels. More recently, waste oil has become known for its ability to be refined into biodiesel fuel. The waste oil which generally requires proper disposal could be an additional non-edible oil source for fuel. It can be hydroprocessed after simple filtration to remove any food particles remaining in the oil after cooking. It is necessary to study in detail how the vegetable oils could be hydrotreated with petroleum − derived feedstocks such as gas oil in the existing petroleum refinery infrastructure to produce diesel fuel with better product properties and maximum yield with little modification in the existing conditions in refineries to make the process economically attractive. We report the results for hydrotreating mixtures of gas oil and waste vegetables oil, by varying different process parameters in the range varied in a typical diesel hydrotreater (DHDT) unit, and discuss strategies as to how gas oil and vegetables oil could be hydroprocessed in the same reactor within a petroleum refinery.

2.   Material and methods

2.1.   Feeds and their properties

Gas oil was supplied by Mathura Refinery, India and its properties are reported in Table 1. Waste restaurant *G. max* (soya) oil was used for this study after filtration to remove solid residues and was characterized by various techniques described later in Section 2.4, and the properties are listed in Table 1. The species were harvested in the Indian subcontinent (geo-coordinates: 22°N, 72°E). The oil is extracted from the beans (∼18%yield) and refined. The entire oil milling process generally includes: cleaning, sieving, hulling, separation, cracking, particle making, frying, softening, flaking, drying, and expelling oil materials. Extraction of oil from the prepared material is done with the aid of a food-grade solvent hexane. Distillation is done to remove the solvent from the extracted oil. Final step is recovery of solvent, which is reused. The commercial refined oil (Ruchi Soya Industries Limited, India) was used for cooking in a typical restaurant for deep-frying. The used oil, after it was declared unfit for cooking in the restaurant, was filtered (Whatman No. 41) and used in this work. The oil had composition of 10.8% palmitic acid (C16:0), 3.8% stearic acid (C18:0), 28.7% oleic acid (C18:1), 49.9% linoleic acid (C18:2) and 6.8% linolenic acid (C18:3). The acid value (TAN) and viscosity of fresh soya oil was 0.50 and 4.15 respectively, while that of waste cooking oil has slightly higher TAN (0.9) and higher viscosity (4.45). Slight difference in the properties makes both the kind of oils equally suitable for processing. Moreover, hydroprocessing is not sensitive to free fatty acid (FFA) content. Using waste oil has the advantage of being a cost-effective raw material and sidesteps food versus fuel issue.

2.2.   Catalysts and their characterization

Waste *G. max* (Soya) oil and gas oil mixtures were processed in a fixed bed reactor with sulfided Ni−W/SiO$_2$−Al$_2$O$_3$ and Ni−Mo/Al$_2$O$_3$ catalysts listed in Table 2. The catalysts were prepared by conventional impregnation of the support using an aqueous solution of $(NH_4)_6Mo_7O_{24}$ and $Ni(NO_3)_2$. The support was mixed with the impregnation solution and after stirring for 1 h it was dried at 100 °C and calcined in an air stream at 400 °C for 1 h. N$_2$ adsorption−desorption using a Micromeritics ASAP 2010 instrument over samples evacuated at 350 °C for 4 h was used to determine specific BET surface area (S$_{BET}$) and pore volume. Pore size was calculated from the desorption branch of the adsorption−desorption isotherms by the Barrett−Joyner−Halenda (BJH) method. Ammonia TPD was used to determine the acidity and oxygen chemisorption was used to determine the oxygen capacity.

Feed mixture		Density @ 15 °C (g cm^{-3})	S (μL/L)	N (μL/L)	TAN mg $_{(KOH)}$ g^{-1}	Pour point (°C)	IBP-250 °C	250−380 °C	380 °C-FBP
Gas oil	Soya oil								
100	0	0.8583	1940	125 (63.2)[a]	0.45	12	12.6	86.1	1.3
0	100	0.9148	41.6	n.d.	0.9	−6	−	0.20	99.8
90	10	0.8599	914.3	n.d.	0.5	15	3.7	68.5	27.8
75	25	0.8696	884.3	n.d	0.6	18	5.4	71.8	22.8
60	40	0.8767	689.5	n.d.	0.8	18	7.5	71.9	20.6

Table 1 − Properties of feeds used in the study.

a Basic N.