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Temperature effect on co-hydroprocessing of heavy gas oil–waste cooking oil mixtures for hybrid diesel production

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HIGHLIGHTS

- WCO can be integrated to heavy gas oil hydrotreating without decreasing final product quality.
- WCO content in feedstock favors conversion but requires higher hydrogen consumption.
- Increased temperatures and WCO percentage in feedstock favor saturation.

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ABSTRACT

The effect of temperature on hydrotreating of heavy gas oil (HGO)–waste cooking oil (WCO) mixtures was studied. Three different types of feedstock were studied, 100% HGO, 90/10 HGO/WCO and 70/30 HGO/WCO. Temperature is the most dominant operating parameter which defines catalyst performance as well as catalyst life. In this analysis, a hydrotreating temperature range of 310–350 °C was explored via a series of three experiments (310 °C, 330 °C and 350 °C). Several parameters were considered for evaluating the effect of temperature including heteroatom removal, conversion, pour point, hydrogen consumption and saturation of double bonds. For all experiments the same commercial hydrotreating catalyst was utilized ($NiMo/Al_2O_3$), while the remaining operating parameters were kept constant (pressure = 1200 psig, LHSV = 1.0 h^{-1}, H_2/Oil ratio = 505.9 nl/l, liquid feed = 40 ml/h, and gas feed = 21804 ml/h).

1. Introduction

Biofuels are becoming a prominent source of transportation energy, especially since their production process ensures sustainability and economic growth. The literature contains hundreds of references of biodiesel production from a wide variety of feedstocks. At present, however, the dominant feedstocks are soybean oil in the USA [1,2], rapeseed oil in Europe [3], and palm oil in Southeast Asia [4]. Other vegetable oils having real or potential commercial interest as biodiesel feedstocks include canola [5], coconut, corn, *jatropha* [6], safflower, and sunflower [7,8]. Furthermore residual liquid biomass such as animal fats and waste cooking oil [9,10] represent significant markets for biodiesel in many locations.

The aim of EU's biofuel directive is to raise the proportion of biofuels and other renewable fuels to 10% of the total transportation fuel needs by 2020 [11]. Oil companies have already started to investigate options for using existing petroleum refineries infrastructure to convert biomass-derived feedstocks into fuels and chemicals including catalytic hydrotreating and hydrocracking [12]. One such process is catalytic hydrotreating, which is used in the petroleum refinery to remove S, N and metals from petroleum-derived feedstocks including heavy gas–oil or vacuum gas–oil [13]. The heteroatom removal functionality of catalytic hydrotreatment has been extended for the oxygen removal of various vegetable oils [14–16] as well as waste cooking oil [9,10].

However, only until recently the option of co-hydroprocessing of petroleum fractions with lipid feedstocks has been investigated. Templis et al. have studied the effect of the presence of triglycerides on the catalytic hydrodesulfurization (HDS) of gasoil and the hydrogen consumption reactions during catalytic hydroprocessing of gas oil–palm oil mixtures at conventional hydrotreatment conditions over a commercial $CoMo/\gamma\text{-}Al_2O_3$ catalyst [17]. Furthermore, studies on hydroprocessing sunflower oil and a straight run gas oil mixtures in the diesel fuel range over sulfide

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NiO(3%)–MoO_3(12%)–γ-Al_2O_3 incorporating 0, 15 or 30 wt% zeolite beta have been carried out by Sankaranarayanan et al. [18]. Moreover, catalytic hydroprocessing of cottonseed oil in petroleum diesel mixtures for production of renewable diesel was also studied by Sebos, providing satisfactory results concerning the use of the existing petroleum refinery infrastructure for vegetable oil conversion to diesel fuel [19]. Equally important is hydrocracking of vacuum gas oil–vegetable oil mixtures for biofuels production, as studied by Besergianni et al. [20].

This paper investigates the effect of temperature on catalytic hydrotreatment of heavy gas oil (HGO)–waste cooking oil (WCO) mixtures for biofuel production. Three different types of feedstock were studied, 100% HGO, 90/10 HGO/WCO and 70/30 HGO/WCO. In this analysis, a hydrotreating temperature range of 310–350 °C was explored via a series of three experiments (310 °C, 330 °C and 350 °C). Several parameters were considered for evaluating the effect of temperature including heteroatom removal, conversion, pour point, hydrogen consumption and saturation of double bonds. For all experiments the same commercial hydrotreating catalyst was utilized (NiMo/Al_2O_3).

2. Materials and methods

For this study, a small-scale hydroprocessing pilot plant of CPERI/CERTH was employed. This hydroprocessing unit can be used for both hydrotreating and hydrocracking reactions at high pressures and temperatures. It mainly consists of a liquid feed system; hydrogen feed system, a fixed-bed reactor system and a product separation system. The whole unit resembles commercial ones, as it is semi-automated with the operating parameters being automatically controlled. User-friendly software allows the easy handling and control of the unit. The reactor dimensions are 704 mm height, 15.59 mm diameter and 132.44 ml volume.

For this study three different types of feedstock were utilized, pure HGO and two HGO/WCO mixtures (90/10 and 70/30) without any additives. After the liquid feedstock is mixed with high pressure hydrogen, it enters the fixed-bed reactor where hydrotreating and/or hydrocracking reactions take place. The product exits the reactor in a mixed gas–liquid phase, is cooled and finally flashed via a high pressure-low temperature separator, where the gas and liquid phases separate. The experiments were conducted at three temperatures 310 °C, 330 °C and 350 °C and total pressure of 1200 psig corresponding to liquid hourly space velocity (LHSV) of 1 h^{-1}.

For the evaluation of the hydrotreating effectiveness, the total liquid product is collected daily and several analyses take place in the analytical laboratory of CPERI. These analyzes include simulated distillation, density, sulfur and nitrogen, carbon and hydrogen. The gas product is chromatographically analyzed offline.

A commercial NiMo/γ-Al_2O_3 catalyst was employed for all experiments without any manipulation (eg. extrudate breaking). The original extrudates were diluted with SiC to achieve good heat and mass transfer to avoid feed channeling. The catalyst used in this study is pre-sulfided according to the catalyst provider's recommended procedure. Each experiment (condition) is considered complete when the reactions reach steady state, usually after 3–4 days on stream. This is verified by monitoring the product density and sulfur content in the liquid product daily. Once these properties are stabilized, the individual effects of each experiment are considered stable and the study of that condition complete. The product collected during the last day of each study is analyzed in detail, as it represents that particular condition.

Liquid samples were analyzed with DMA4500 for density. Simulated distillation of the hydrotreated products were carried out using an Agilent 6890N (Gas Chromatograph) according to the ASTM D-7213 SIMIDIS procedure. The concentration of sulfur in the feed and liquid products was determined by ASTM D5453-93 analysis while the concentration of nitrogen in the feed and liquid products was determined by ASTM D 4629. Finally the reaction gases were analyzed with a Gas Chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD).

To conclude, WCO was collected from local restaurants as well as households, after extensively being used for frying. Before mixed it with HGO, the WCO was filtered via a regular sieve to remove any food particles remaining in the oil after frying. The WCO that was used in the experiments consist of a mixture of used cooking oil coming from local restaurants and homes. The triglycerides content of the WCO employed in the experiments is given in Table 3.

3. Results

For this study three experiments at a temperature range of 310–350 °C were conducted in order to study the effect of reactor

Table 1
Quality comparison of hydrotreatment products at different temperatures. All experiments were conducted at P = 1200 psig, LHSV = 1.0 h^{-1} and H_2/oil = 505.9 nl/l (HGO/WCO 100/0, 90/10, 70/30).

	310 °C			330 °C			350 °C		
	100/0	90/10	70/30	100/0	90/10	70/30	100/0	90/10	70/30
Density (kg/m^3)	0.866	0.858	0.84	0.862	0.855	0.837	0.853	0.845	0.831
S (wppm)	2150	1770	1270	515.3	440	271.9	39.2	71	51
N (wppm)	246.8	115.3	94.21	28.5	19.55	12.11	0.99	6.77	2.65
H (wt%)	12.45	13.881	14.2	12.93	13.01	14.31	13.53	14.27	14.5
C (wt%)	85.9	86.36	85.81	85.51	86.66	85.73	84.33	87.33	86.19
O (wt%)	1.41	~0	~0	1.5	~0	~0	2.136	~0	~0
IBP (°C)	158	160	161	155	149	157	134	149	119
5% (°C)	241	244	256	236	240	252	214	241	229
10% (°C)	277	279	286	272	275	279	255	275	270
20% (°C)	313	307	305	309	304	304	297	305	303
30% (°C)	334	323	317	331	320	312	322	320	308
40% (°C)	351	344	322	348	341	322	342	341	320
50% (°C)	364	359	340	362	358	336	358	358	331
60% (°C)	376	373	359	374	371	358	371	372	354
70% (°C)	388	385	376	386	384	374	383	384	372
80% (°C)	400	399	392	399	398	391	397	398	389
90% (°C)	416	415	411	415	414	410	413	415	409
95% (°C)	428	427	425	427	427	424	426	427	424
FBP (°C)	459	457	488	457	467	477	457	468	513