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Catalytic cracking of vegetable oil with metal oxides for biofuel production

Zerihun Demrew Yigezu, Karuppan Muthukumar *

Department of Chemical Engineering, A.C. Tech. Campus, Anna University, Chennai 600025, India

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ABSTRACT

This study presents the utilization of metal oxides for the biofuel production from vegetable oil. The physical and chemical properties of the diesel-like products obtained, and the influence of reaction variables on the product distribution were investigated. Six different metal oxides (Co_3O_4, KOH, MoO_3, NiO, V_2O_5, and ZnO) were employed as catalysts and the results indicated that the metal oxides are suitable for catalyzing the conversion of oil into organic liquid products (OLPs). The maximum conversion (87.6%) was obtained with V_2O_5 at 320 °C in 40 min whereas a minimum conversion (55.1%) was obtained with MoO_3 at 390 °C in 30 min. The physical characteristics of the product obtained (density, specific gravity, higher heat value, flash point and kinematic viscosity), were in line with ASTM D6751 (B100) standards. The hydrocarbons majorly present in the product were found to be methyl and ethyl esters. Furthermore, OLPs obtained were distilled and separated into four components. The amount of light hydrocarbons, gasoline, kerosene and heavy oil like components obtained were 18.73%, 33.62%, 24.91% and 90.93%, respectively.

1. Introduction

The rapid industrialization, growth of global economy, and increase in population significantly enhanced the demand for fossil fuels. On the other hand, the depletion of fossil fuel reserves motivates researchers to find out alternative energy sources. Biofuels, find attraction worldwide as a blending component or a direct replacement for fossil fuels [1,2]. Moreover, the production of biofuel from vegetable oils has become more impressive option because of their environmental benefits [3]. However, bio-oils are highly oxygenated, acidic, corrosive to common metals, chemically and thermally unstable, as well as non-miscible with petroleum fuels [4], which make them difficult to use directly in various devices, especially in internal combustion engines [5].

The vegetable oils are converted into biofuels, primarily by transesterification/esterification. This process can be catalysed using enzymes [6–9] or using chemical catalysts [10–14]. Few catalysts are widely accepted and utilized commercially. However, the problems need to be solved include solvent and heat sensitivity, high cost of enzyme, and the need of alcohol for transesterification. The production cost of biodiesel is the main hurdle, which limits the commercialization of this method. Catalytic cracking is an alternative route for the production of biofuels from vegetable oils and animal fats [15]. Catalytic cracking is a simple and effective method for biofuel production. The operational cost associated is low and the technology is compatible with available infrastructures. Importantly, flexibility regarding the sources of oil/fat and the product obtained matches with engines and fuel standards [1]. The other advantage is that enzymatic or chemical transesterification is used to produce only biodiesel, which requires longer reaction time whereas catalytic cracking can be used for the production of kerosene, gasoline and diesel in a faster manner [16]. The use of catalysts for thermal cracking of vegetable oil results in lower temperature requirement, higher conversion rate, less residence time and better quality of the derived product [16]. The catalysts mainly used include metal oxides, molecular sieves, activated alumina and sodium carbonate.

The metal oxides find extensive applications in various catalytic processes due to their unique properties such as high specific surface area, strong base strength and high concentration of base sites [17]. These features of metal oxides are related to structure, type of bond between the metal and oxygen, and presence of basic and/or acid sites. Catalytic properties of metal oxides arise from adsorption of reactants on unsaturated metal sites and/or oxygen atoms, followed by addition or elimination of hydrogen and/or oxygen [18]. These structural features of metal oxides are the primary

* Corresponding author. Tel.: +91 44 22359153; fax: +91 44 22352642.
E-mail addresses: muthukumar@annauniv.edu, chemkmk@gmail.com (K. Muthukumar).

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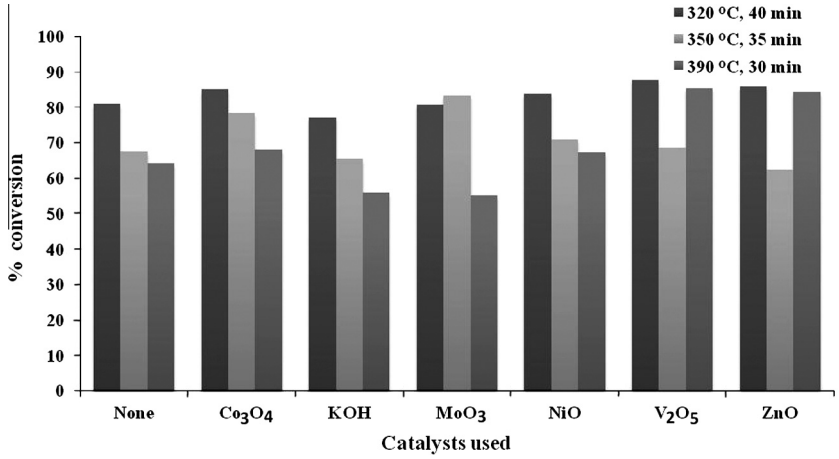

Fig. 1. The effect of various catalysts on % conversion at different temperature and residence time.

motives for utilizing them as catalysts [19–22]. Cobalt oxide (Co_3O_4) has hollow structure and novel properties while MoO_3 has layered structure with ease of Mo(VI)/Mo(V) coupling. Catalytic activity of V_2O_5 in the partial oxidation of hydrocarbons is related to the presence of vanadyl group (V=O) and its selectivity depends on the nature of the support, pretreatment conditions, and the mode of dispersion of vanadium on the support surface [23]. Zinc oxide is an ideal catalyst for the transesterification since it contains both acidic and basic sites. The role of support is to provide higher surface area through the existence of pores where metal particles can be anchored [24]. It can also help to minimize mass transfer limitations in liquid phase reactions.

The potential use of metal oxide catalysts for biofuel production is evident from the literature. They are successfully used for: hydrocracking of vegetables feedstock [25]; for the production of motor fuel from pretreated Hungarian sunflower oil [26]; and selective catalysis of synthetic bio-oil for the production of phenol and light phenolics [27].

The foregoing analysis indicates that further analysis of catalytic cracking of vegetable oils is required. The difference in the distribution of final products obtained with the use of these catalysts depends on reaction variables such as reactor design, catalyst type, residence time, reaction temperature, collection procedure and analytical techniques. This necessitates further testing of metal oxides, detailed characterization of products and scale-up of production. Therefore, this study was carried out with the aim of testing the potential use of selected metal oxides for the catalytic cracking of vegetable oil and investigating the effect of temperature and residence time on the conversion and product distribution.

Table 1
Characteristics of OLPs synthesized at 390 °C and 30 min residence time.

Characteristics	Catalysts used							ASTM (B100)
	None	CO_3O_4	KOH	MoO_3	NiO	V_2O_5	ZnO	
Density (kg/m^3) at 15 °C	872.2	868.7	870.3	869.6	864.8	870.2	880.0	874.7
Specific gravity (kg/l) at 15 °C	0.88	0.87	0.87	0.87	0.86	0.87	0.88	0.88
Higher heat value (MJ/kg)	41.32	41.65	41.63	41.43	41.80	41.60	41.32	39.37
Flash point (°C)	169.6	179.4	167.8	171.4	176.5	178.7	167.0	100–170
Kinematic viscosity (mm^2/s) at 40 °C	3.58	4.23	3.87	3.19	3.40	3.48	3.77	1.9–6

Table 2
Characteristics of OLPs synthesized at 350 °C and 35 min residence time.

Characteristics	Catalysts used							ASTM (B100)
	None	CO_3O_4	KOH	MoO_3	NiO	V_2O_5	ZnO	
Density (kg/m^3) at 15 °C	881.2	883.1	875.6	875.2	868.9	873.4	878.1	874.7
Specific gravity (kg/l) at 15 °C	0.88	0.88	0.88	0.88	0.87	0.88	0.88	0.88
Higher heat value (MJ/kg)	41.12	41.40	41.30	41.57	41.59	41.41	41.21	39.37
Flash point (°C)	155.5	170.3	164.0	173.8	177.4	169.2	171.8	100–170
Kinematic viscosity (mm^2/s) at 40 °C	3.65	3.70	3.72	3.29	3.76	3.72	3.67	1.9–6

Table 3
Characteristics of OLPs synthesized at 320 °C and 40 min residence time.

Characteristics	Catalysts used							ASTM (B100)
	None	CO_3O_4	KOH	MoO_3	NiO	V_2O_5	ZnO	
Density (kg/m^3) at 15 °C	865.2	876.4	867.8	872.1	877.0	877.3	875.6	874.7
Specific gravity (kg/l) at 15 °C	0.86	0.88	0.87	0.88	0.88	0.88	0.88	0.88
Higher heat value (MJ/kg)	41.8	41.54	41.43	41.26	41.45	41.34	41.64	39.37
Flash point (°C)	188.7	173.6	169.7	168.1	174.4	168.7	178.8	100–170
Kinematic viscosity (mm^2/s) at 40 °C	4.21	3.73	4.01	3.41	3.80	3.89	4.10	1.9–6