



Biofuel production by catalytic cracking of sunflower oil using vanadium pentoxide



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 kinetic aspects of organic liquid products (OLP) synthesis from sunflower oil by catalytic cracking. A three-lump reaction kinetic model and Arrhenius equation were used to estimate the reaction constants and activation energy values. The effect temperature and catalyst concentration on % conversion and product distribution were analyzed. The maximum OLP formation (92.1%) was obtained at 628 K with 1.5 wt.% catalyst in 40 min. The data predicted by 3-lump kinetic model were well consistent with the experimental values. The smaller value of reaction constant obtained for the conversion of OLP into gas and coke indicates the presence of little secondary reactions. The lower activation energy required to convert the oil into OLP implied the selectivity of the catalyst towards OLP formation. The measured physical properties of the OLP were within/close to the required limits of ASTM D6751 (B100) specifications. FTIR and GC–MS analysis identified aliphatic ester and their derivatives as major constituents of the OLP. Variations in the fractional distillates of OLP indicate the influence of reaction conditions not only on % conversion but also on product distribution.

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1. Introduction

The depletion of fossil fuel reserves and its contribution to greenhouse effect attract the development of non-petroleum, renewable and non-polluting fuels [1]. Biofuel is an alternate fuel and can be used in automobiles without any modification of the engine [2]. The advantages include adaptability with existing filling-fuel stations, biodegradability and environmental friendly [3]. Enzymatic/chemical methods are preferred for biodiesel production, but the high cost of commercially available enzymes restricts large scale applications of enzymatic method [4–6]. Enzyme inactivation caused by excess methanol and glycerol [7–10] is the other hurdle that affects the yield of enzymatic methanolysis. Chemical catalysts on the other hand provide high conversion of triglycerides to methyl esters and require less reaction time [11]. However, the most popular alkali-catalyzed transesterification requires highly refined vegetable oil, and water and free fatty acid (FFA) content in the reaction system must not exceed 0.3% and 0.5%, respectively [12].

Catalytic cracking of vegetable oils has become more attractive for biofuel production due to its lower operational costs, compat-

ibility with available infrastructures and flexibility with respect to the sources of oil/fat [13]. Catalysts used include metal oxides, molecular sieves, activated alumina and sodium carbonate. The characteristics of active transesterification catalysts include high specific surface area, strong base strength and high concentration of base sites [14]. In metal oxide catalysts, these features are related with the structure, type of bond between metal and oxygen, and presence of basic and/or acid sites on the surface. Vanadate compounds are active and stable in oil transesterification [15]. 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 support, pretreatment conditions, and mode of dispersion of vanadium on the support surface [16]. Prior to the current investigation, the potential uses of six metal oxides (Co_3O_4 , KOH , MoO_3 , NiO , V_2O_5 , and ZnO) were studied for conversion of sunflower oil into organic liquid products (OLP) [17]. Vanadium pentoxide gave a better OLP yield under operating conditions tested, and the final product distribution was highly dependent on the reaction variables such as cracking temperature, catalyst concentration and residence time.

The study of reaction kinetics involving catalytic cracking process is done based on lumping strategy in which similar components are grouped into a few “cuts” [18]. The more lumps a model includes, the more kinetic parameters need to be estimated, and consequently, the more experimental data are required [19]. Thus,

* Corresponding author. Tel.: +91 44 22359153; fax: +91 44 22352642.

E-mail addresses: muthukumar@annauniv.edu, chemkmk@gmail.com (K. Muthukumar).

it is necessary to establish a model that can give the key kinetic information. The present study is intended to optimize the reaction and develop a reaction kinetic model for catalytic cracking of vegetable oil into OLP, gas and coke with the use of V_2O_5 as a catalyst. The effects of temperature and catalyst concentration on the fractional distillates of the OLP were also analyzed.

2. Materials and methods

2.1. Materials

Commercial grade sunflower oil was purchased from a local shop and used without any further treatment. The fatty acid composition of the oil was; oleic acid (58.4%), linoleic acid (23.5%), palmitic acid (9.3%), stearic acid (7.7%) and pentadecanoic acid (1.0%). The catalyst (V_2O_5) and alumina ($\alpha-Al_2O_3$) were supplied by Fisher scientific. The alumina used in this study helps to minimize mass transfer limitations during the reaction process. Since the cracking process takes place at higher temperature, a high pressure will be developed inside the reactor. The pressure will physically spread the catalyst particle over the surface of the alumina and more active sites (catalyst pores) will be exposed. The exposition of more catalyst pores will facilitate the mass transfer process from the external pore mouth to the internal catalyst surface. Particularly, if the catalyst is intended for repeated use, calcination is required to reactivate the catalyst in between the cycles; in that case the alumina can serve as a support. Alumina was used to reduce the mass transfer imitations. The temperature was controlled using a digital temperature controller working in conjunction with two thermocouples with an accuracy of $\pm 2^\circ C$.

2.2. Cracking conditions

The cracking was carried out using a round bottom, three-necked, 250 ml capacity Borosil flask equipped with Liebig Drip Tip condenser. Initially, 0.5 g of alumina was placed in the flask and it was added with appropriate amount of oil and catalyst. One of the thermocouples was dipped into the contents of the flask while the other was hanging above through the respective side neck to measure temperature of the liquid content and vapor leaving the flask. The heating mantle was allowed to heat the contents of the reactor for a specified length of time. The condensate from the condenser was collected in the receiver kept in the ice bath for further cooling. The OLP separated from the rest of the condensate with careful filtration was weighed. The % yield of OLP, and gas and coke (g+c) was calculated using the following equation:

$$\% \text{yield} = \left(\frac{\text{amount of desired product}}{\text{amount of initial oil used}} \right) \times 100 \quad (1)$$

where, desired product could be OLP or g+c formed during the process.

2.3. Reaction kinetics model

A three-lump model, proposed by Weekman and Nace [20] was used to develop the catalytic cracking kinetic model of the oil with some modification (first order reaction kinetics was adapted). The model can be represented as shown in Fig. 1. Based on three-lump model, the cracking rate (r_0) of the oil can be expressed as:

$$r_0 = -\phi_1 (k_1 + k_2) C_0^n \quad (2)$$

where, k is reaction kinetics constant and n is the kinetic order.

In the present study, formation of OLP (r_{OLP}) and gas + coke (r_{g+c}) were defined as follows, respectively:

$$r_{OLP} = k_1 \phi_1 C_0 - k_3 \phi_2 C_{OLP} \quad (3)$$

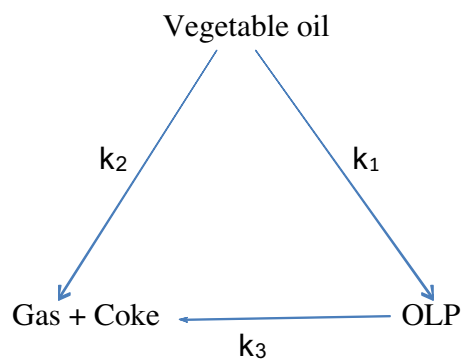


Fig. 1. Three-lump kinetic model k_1 , k_2 and k_3 are the reaction rate constants.

$$r_{g+c} = k_2 \phi_1 C_0 + k_3 \phi_2 C_{OLP} \quad (4)$$

where, C_0 is the concentration (wt.%) of initial oil used in the reaction mixture, C_{OLP} is the wt.% of the OLP collected per initial oil used and ϕ is the reduction in catalyst activity with time. Since the same catalyst applied for a constant reaction time, ϕ_1 and ϕ_2 are assumed to be the same.

The independent reaction variables such as cracking temperature (603, 628 and 653 K) and catalyst concentration (1.0, 1.25, 1.5, 1.75 and 2.0 wt.%) were varied during the cracking of oil at a constant residence time of 40 min. The reaction conditions were selected based on our previous observations in which temperature and catalyst concentrations were the primary reaction determining factors. The OLP and g+c under each condition were used to find out the kinetic parameters. The non-linear regression analysis based on Levenberg–Marquardt algorithm was applied to determine k_1 , k_2 and k_3 . The rate constants were used to calculate the activation energy and frequency factor from the Arrhenius equation:

$$k = A e^{-E_a/(RT)} \quad (5)$$

where, A is frequency factor, T is cracking temperature in K, E_a is the activation energy and R is the universal gas constant.

2.4. Product analysis

Specific gravity (SG) and kinematic viscosity (V) were measured using hydrometer with DN range of 0.850–0.900 and Ostwald viscometer, respectively. The important diesel properties such as higher heating value (HHV) and flash point (FP) were estimated following appropriate procedures, and compared with ASTM D6751 (B100).

Sample of OLP was analyzed using FTIR spectrometer (PerkinElmer Infrared model 337) to predict the type of hydrocarbon compounds synthesized mainly. Chemical composition of the OLP was checked using GC–MS (JEOL GCMATE II GC–MS with data system, double focusing instrument; Conditions: capillary column (HP5); MS secondary electron multiplier (detection); evaporation $10^\circ C/min$; oven temperature 50 – $250^\circ C$ and helium was used as carrier gas at a flow rate of 1.5 ml/min).

2.5. Fractional distillation

The OLPs were distilled and separated into four major components based on the distillation temperature (DT) intervals of petroleum: $DT < 80^\circ C$ = light hydrocarbon; $80^\circ C \leq$ gasoline $< 140^\circ C$; $140^\circ C \leq$ kerosene $< 200^\circ C$; and heavy diesel $\geq 200^\circ C$. The distillation temperature intervals were reported to give hydrocarbon fractions having similar properties with respective petroleum distillates [21,22]. The amount of each

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