



Bound cleavage at carboxyl group-glycerol backbone position in thermal cracking of the triglycerides in sunflower oil



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ABSTRACT

Bound cleavage at carboxyl group-glycerol backbone position of triglyceride of sunflower oil during the thermal cracking reaction was studied. Required experiments were performed in a continuous tubular reactor at atmospheric pressure. Experimental results showed that cracking at each bond of $-OC-O-C$ depends on the temperature. At low process temperatures, decarboxylation was enhanced, while at high temperature more fatty acids were formed. When liquid products were fractionated into some light to heavy cuts, the distribution of fatty acids was observed. Concentration of COOH group in the cuts showed that at the cracking conditions, carboxylic acid head of fatty acids was more stable than their hydrocarbon chain, so the second bound cleavage step had been taken place along the hydrocarbon chain and lighter fatty acids were formed. As a result, a more accurate mechanism for thermal cracking of triglycerides is recommended. The presented mechanism would help the experimentalists to have an accurate prediction of the products for thermal cracking process of triglycerides.

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1. Introduction

Increasing of crude oil prices and environmental effects of utilizing fossil fuels, such as global warming and air pollution, have increased interests in using renewable fuels. There are many sources of renewable energy, but they have very limited applications. The transportation sector requires sources of renewable energy such as common liquefied fossil fuels. Vegetable oils have a similar molecular structure to crude oil and common fuels. Therefore, today attentions for upgrading of vegetable oils to biofuels as renewable sources of energy, has been increased. These sources have some benefits to common hydrocarbon based fuels. They are almost CO₂ neutral [1] and release a little sulfur, which are major pollutants emit from common fuels and biodegradable [2,3]. Vegetable oils cannot be used directly as a fuel, because they lead to problems such as carbon deposits, oil ring sticking and gelling of the lubricating oil [4–6]. To tackle these problems they must be converted to the form and properties similar to the ordinary petroleum fuels. Some methods such as transesterification and cracking have been recommended for this purpose. Biodiesel, which is produced during the transesterification reaction of vegetable oils with an alcohol such as methanol, has performance and emission

characteristics close to the petroleum diesel [7]. Biodiesel applications are not only limited to diesel engines, but also has limited cold properties that cannot be used in the cold climate regions. Therefore, other modification methods have been required to produce lighter biofuels like jet fuel and gasoline. Many researchers have tried to convert Vegetable oils to these types of fuels through cracking processes [8–16], which are currently used in the petroleum and petrochemical industries to convert heavy cuts to light ones. Vegetable oils or fats are more expensive than crude oil [17,18]; therefore, cracking process must work at the highest yield of production and quality of biofuels. For these purposes the process must be well known.

Many researchers have studied these processes to achieve some knowledge about yields and component distribution [8,13–15,19–28]. Several of them have tried to improve the fuel property of organic liquid products [7,11,12,29–32]. One of the fields of study is the kinetic mechanism of thermal cracking reaction. The goal of these researches is to explain how the molecules are cracked, how molecules of products are formed and which molecules and types of fuel products must be more expected [2,15,25,33,34,41]. This knowledge helps us to select the best feed, process, and process conditions.

Prediction of a cracking mechanism for the reactions is an important feature of the process. During the cracking process bound cleavage takes place along the reactant molecules and light ones are produced. Paraffins, olefins, aromatics, etc. are products

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of cracking of hydrocarbons. The severity of the cracking and characteristics of the reactants determine the size and characteristics of the product molecules. In all cracking processes some of the products are desired which must be maximized. In the cracking of vegetable oils, fats and triglycerides the main goal is the liquid products which will be used as a fuel. Many studies have been conducted on the decomposition of triglycerides at high temperature [35–39]. Pyrolysis of vegetable oils starts about 300 °C and fatty acids and acroleins are formed. The cracking is started when temperature rises to 400–500 °C, and short chain hydrocarbons will be produced [35].

The mechanisms of thermal cracking for saturated triglycerides have also been studied by some researchers. A reaction scheme has been proposed for the pyrolysis of saturated triglycerides [5,16,29,45,46]. The mechanism which includes 16 reaction steps have been shown in Fig. 1. According to this reaction pathway at first step triglycerides decompose to fatty acids, acrolein and 2-propenal through reaction (1). Fatty acids rapidly cracks to linear hydrocarbons, ketonize to heavier ketones, H₂O and CO₂ according to the reaction set (2). Reaction set (3) defines decomposition of acroleins, 2-propenal and ketones already formed through reaction set (2). Finally, several general reactions have been suggested by the authors to represent how other products like paraffins, olefins, diolefins, acetylenics, cyclic hydrocarbons, aromatics and coke are formed.

Based on the reaction pathway of Fig. 1 and on the results presented by Greensfelder et al., Alencar et al. [40,41] also proposed a scheme for the cracking of saturated triglycerides. Fig. 2 shows their suggested radical reaction pathway in which they recommend more details for formation of light and heavier alkanes and alkenes [5,16].

Since vegetable oils mainly contain unsaturated triglycerides, the mechanism of Fig. 2 cannot cover all the possible reactions for them. Therefore, the mechanism presented in Fig. 3 has been recommended [5,16,42]. According to this mechanism at the first step an unsaturated fatty acid radical is separated from a triglyceride molecule and then it is cracked along its carbon chain before a carboxyl group which results smaller fatty acid radicals and some paraffinic and olefinic hydrocarbons are formed. Fatty acid radicals absorb hydrogen atoms and will be converted to a molecule.

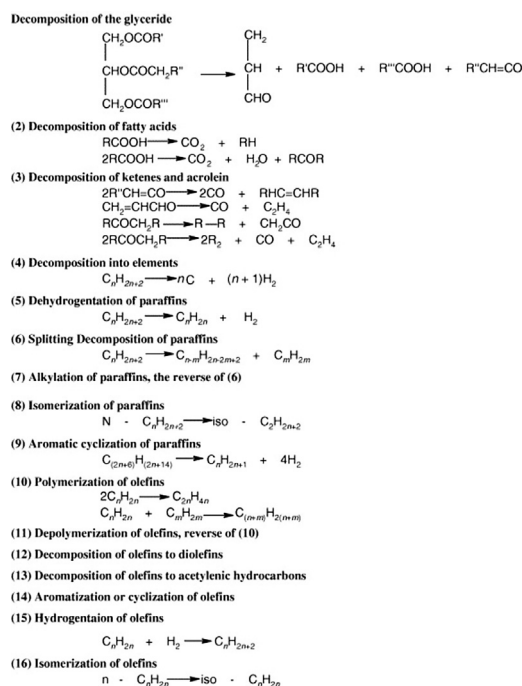


Fig. 1. A reaction mechanism for thermal cracking of saturated triglycerides [5,16,29,45].

Then a CO₂ molecule is removed and an alkane is formed. Another recommendation of this mechanism is bond cleavage around the unsaturation of carbon chain at β position, so as a butadiene molecule is formed. Butadiene is then converted to aromatics through Diels-Alder reaction by addition of an ethylene. Formation of acrolein has also been detected in the pyrolysis of sunflower oil as a source of unsaturated fatty acids [16].

Fig. 4 shows another recommended reaction pathway for thermal cracking of canola oil [43]. This mechanism has been developed from the previously suggested mechanism by others [29,37,39,41,42,44]. The reaction scheme tries to explain how heavy oxygenated compounds including ketones, aldehydes and

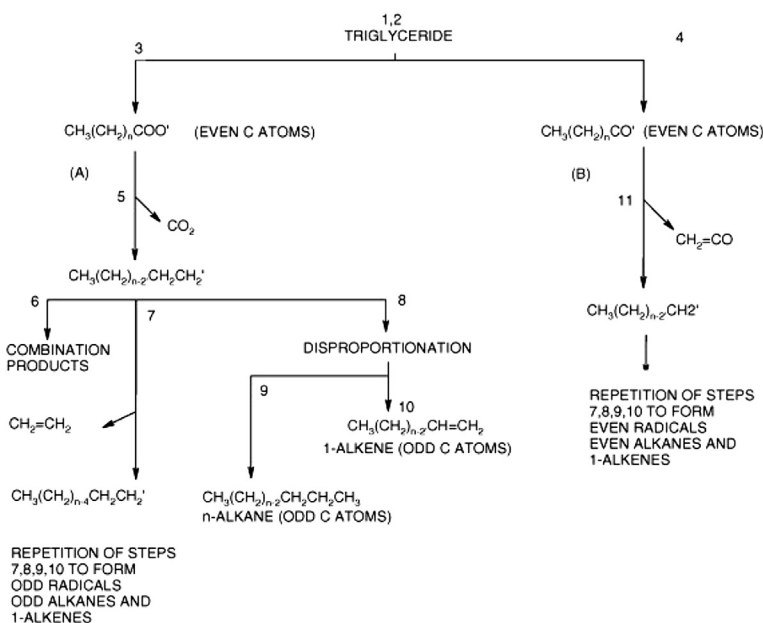


Fig. 2. Radical mechanism for thermal cracking of saturated triglycerides [5,16].

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