

# Production of Renewable Transportation Biofuels by Thermal/Catalytic Cracking of Triglycerides and Their Methyl Esters

S.M. Sadrameli\*, H. Seifi

Chemical Engineering Department, Tarbiat Modares University, Tehran, Iran

## Introduction

Sharp increase of fossil fuel consumption, depletion of natural resources, and environmental concerns leads to the production of transportation fuels derived from renewable sources which are potentially good alternatives for the conventional fossil-derived fuels. Triglycerides with a molecular network very similar to hydrocarbons are among the alternative energy sources for the production of biofuels via pyrolysis, transesterification, etc. Transesterification of triglycerides in the presence of a catalyst and one alcohol converts them to the fatty acid methyl esters (FAMES). Thermal cracking of triglycerides and their methyl esters can convert them to the smaller molecules of hydrocarbons from which transportation renewable fuels can be produced. This has been an interesting topic for the researchers in the last two decades for obtaining a feasible renewable fuel that can be comparable to the fossil fuels. From the literature review it can be concluded that none of the presented processes can produce a fuel that completely matches the fossil fuel standards. The oxygen content in the fuel is also one of the significant parameters that directly affect the fuel properties. This poster presents some of the results obtained from the study of deoxygenation, and ketonization processes using thermal/catalytic cracking of sunflower oil and its methyl esters for the production of transportation biofuels. Sunflower oil was converted to methyl ester in the presence of KOH through transesterification reaction and was used as a feed for the cracking process. Thermal cracking of sunflower oil and its methyl esters were compared to determine the benefits of transesterification process as a pretreatment step for the triglycerides.

## Materials and Methods

Purified sunflower oil was purchased from the local market and used as a feedstock for the esterification and cracking processes. Fatty acid analysis of the oil has been performed by a GC model PerkinElmer-Claruss 580 with the BPX - BIOD5 column (12 m × 0.32 mm + 2 m × 0.1) with FID detector was used to determine the percentage of fatty acids. Total carboxyl groups of the oil and liquid products are measured by the ASTM D94 and acid values estimated by the ASTM D974. A distillation setup adapted from ASTM D86 is used to distillate liquid products and fractionate into required cuts. Density of the oil and liquid products were measured by a Pycnometer and viscosity was measured by an Ostwald viscometer. The remaining required materials for the analysis such as KOH, HCl, C<sub>2</sub>H<sub>5</sub>OH (99.5 wt.%), CH<sub>3</sub>OH (99.5 wt.%), H<sub>2</sub>SO<sub>4</sub> (98 wt.%), NH<sub>4</sub>NO<sub>3</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, γ-Al<sub>2</sub>O<sub>3</sub>, Na-HZSM5, and isopropyl alcohol, purchased from Merck Company.

Thermal cracking of sunflower oil was carried out in a lab scale setup that is schematically shown in Figure 1. This setup consists of a feed tank and a pumping system, tubular packed bed reactor and its tubular electrical furnace, a condenser, nitrogen purging system, an air injection and flow indicators and temperature control system. The tubular reactor made from quartz with the dimension of 20mm×650mm×1.5mm (OD×L×thk.) was placed vertically and centered in the furnace. The electrical furnace which is 500mm in length and 450mm inside diameter is made by Atra, an Iranian manufacturer company. Reactor tube packed with 60g of ceramic rings with dimension 4mm×5mm×1mm (OD×L×thk.). Furnace temperature is controlled with a control system and the reactor end temperature is measured by a thermocouple and is indicated with a digital indicator. A jacketed glass condenser is used to condense the liquid products and separate them from the gases. Feed and gases flow rates have been measured with two flow indicators. After each run, hot air at temperature of 550 °C was purged to the reactor for one hour for decoking process to clean the reactor.

The main factors that can affect thermal cracking processes are temperature, pressure and feed flow rate. In this work, all the tests were performed at constant atmospheric pressure. This is due to the experimental setup limitations and therefore the effects of pressure have not been studied. Yields, total carboxyl groups and acidity of the organic liquid product (OLP) for the process and its cuts were selected as the process responses. Design Expert 7.0 software was applied to design the required experiments and analysis of the results. A full factorial design at two levels with one replication applied for experiments.

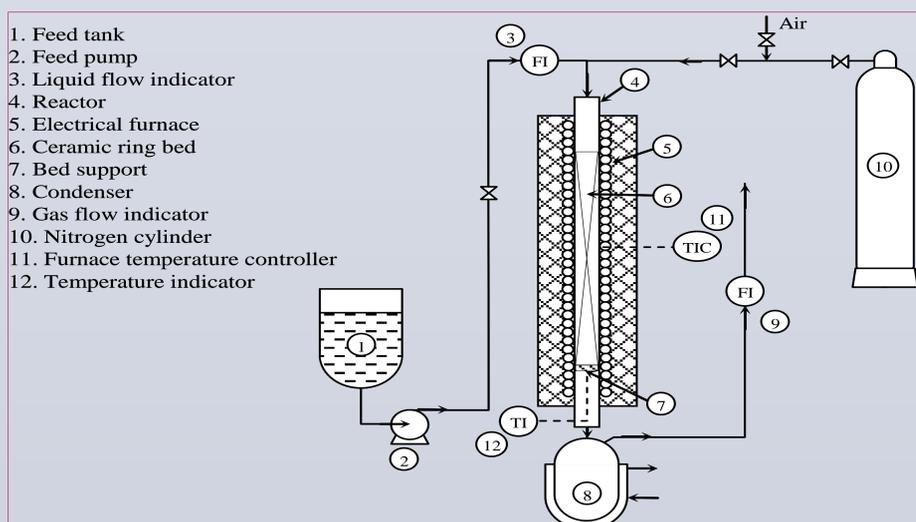


Figure 1. Schematic diagram of experimental setup

## Results and discussions

Thermal cracking of sunflower oil has been performed at two temperatures of 450 and 500°C and for two flow rate of 10 and 20 g/h to investigate the total and different distillation cuts yields and the carboxylic acid values of the products. A comparison has been made for different products produced from catalytic cracking and decarboxylation of sunflower methyl ester. The distillation curves are shown in Fig. 2. The comparison between the cracking products and fossil fuel based kerosene and jet fuel are shown in Fig. 3. As observed from curves in the figure the distillation curves for the final products of deoxygenation and ketonization are very close to the refinery kerosene and jet fuel (JP8).

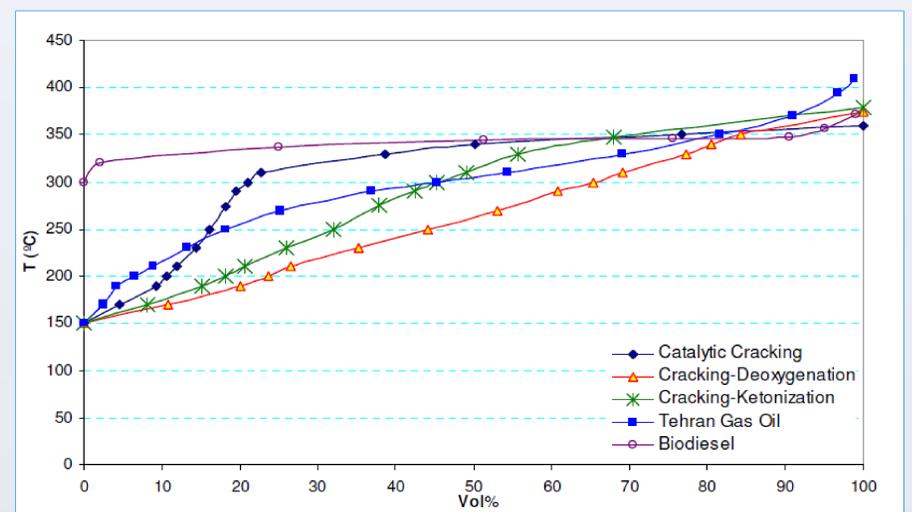


Figure 2. Distillation curves for different cracking products (450 °C, 10 kg/h, LHSV=1 hr<sup>-1</sup>)

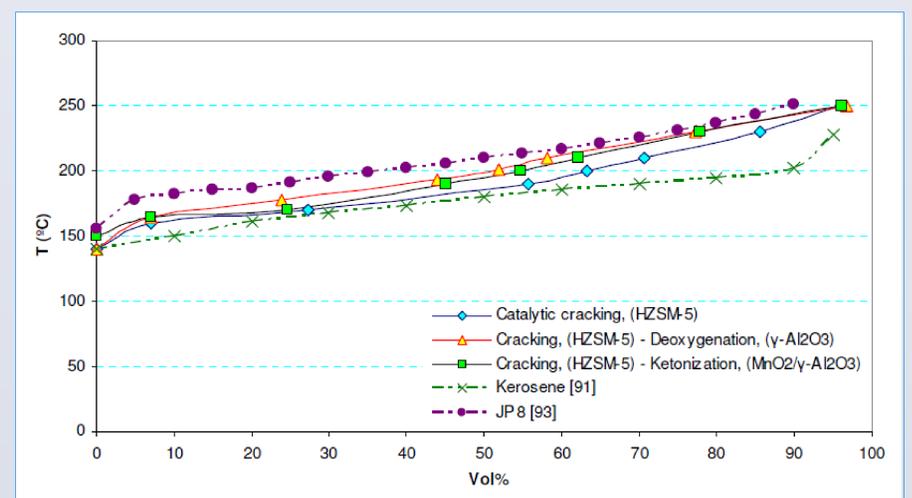


Figure 3. Comparison of the catalytic cracking and refinery kerosene and jet fuel products

## Conclusions

From the experimental results reported above the following conclusion must be summarized:

- Conversion of triglycerides to methyl esters as a pretreatment for thermal cracking can reduce the heavier components and coke deposition on the reactor wall and at the same time increase the yields of the liquid products in comparison to triglycerides cracking.
- The yields of liquid products from thermal and catalytic cracking of triglycerides and their methyl esters are very similar although in thermal cracking instead of water formation from the reactions the heavier components are less in thermal cracking. The catalytic cracking cause partial deoxygenation and the products have more acidity which shows the effects of catalyst on the carboxyl group of methyl esters.
- Deoxygenation of catalytic cracking products using g-Al<sub>2</sub>O<sub>3</sub> leads to the lighter components and makes the fuel very close to the standard fossil fuel.
- Ketonization of catalytic cracking products using MnO<sub>2</sub>/ g-Al<sub>2</sub>O<sub>3</sub> similar to -deoxygenation improves the fuel properties.

The processes can improve the fuel properties such as viscosity, cold properties, distillation curve, heating value and acid number and make the renewable fuel very similar to the crude oil based fuel.

\* Corresponding author: Email: sadrameli@modares.ac.ir