

# High-yield production of fuel- and oleochemical-precursors from triacylglycerols in a novel continuous-flow pyrolysis reactor



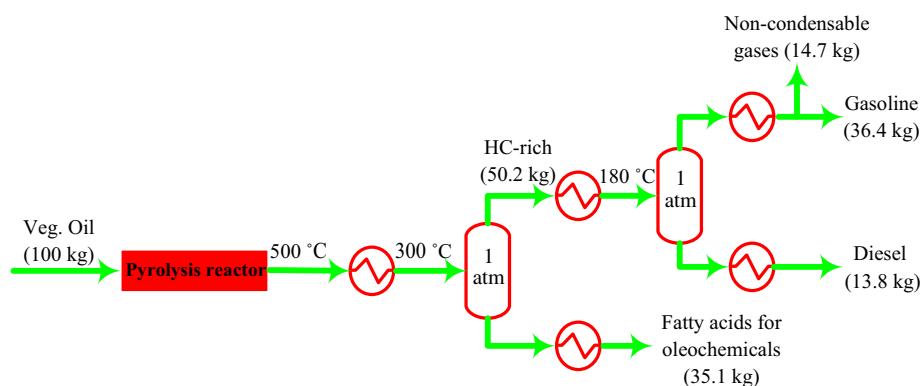
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## HIGHLIGHTS

- Developed and tested novel reactor for continuous pyrolysis of vegetable oils.
- Oil fed via an atomizer - micron-sized droplets rapidly vaporized in the reactor.
- Reactor design allows control of vapor residence time without use of carrier gas.
- Achieved near-theoretical yield of organic liquid products.
- Fuels (gasoline, jet and diesel) as well as enriched oleic acid were produced.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study, conversion of soybean oil was carried out in a continuous pyrolysis system with feed injected through an atomizer. This allowed introduction of micron-sized droplets of oil that could be rapidly vaporized inside the reactor. With this novel design, we were able to achieve feed vapor residence times ( $\tau$ ) of 6–300 s without use of carrier gas, which would significantly reduce the overall cost of pyrolysis. Effects of reaction temperature ( $450 < T < 500$  °C) and  $\tau$  on conversion, product yields and composition were investigated. At the optimum experimental conditions of  $T = 500$  °C and  $\tau = 60$  s, the yield of pyrolysis liquids was as high as 88% (relative to feed mass). Under these conditions, the identified products consisted of 38% hydrocarbons (22%  $C_5$ – $C_{12}$  and 16%  $> C_{12}$ ), 33% long-chain fatty acids ( $C_{16}$ – $C_{18}$ , but primarily oleic acid) and 15% short-chain fatty acids ( $C_6$ – $C_{12}$ ). Upon distillation of the liquid products, the long-chain fatty acids were cleanly separated from the hydrocarbons. Overall, our results demonstrate the feasibility of producing liquid products at high yields, including a wide range of fuels (gasoline, jet and diesel) and enriched oleic acid (for oleochemicals production), using our reactor design for pyrolytic conversion of vegetable oil.

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## 1. Introduction

Energy-dense triacylglycerols (commonly known as triglycerides) from oil seeds or microalgae have the potential to, at least

partially, displace petroleum-derived fuels [1–6]. However, triglycerides cannot be used directly in current combustion engines due to their low volatility and high viscosity [2,7–11]. Vegetable oils, the primary source of triglycerides that are currently used for biofuel production, are typically converted to usable fuels through transesterification [12,13]. In this process, triglycerides react with methanol, usually in presence of a homogenous catalyst (e.g.

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sodium hydroxide or methoxide), to produce a mixture of fatty acid methyl esters (FAMES; commonly known as biodiesel) [14,15]. Since the transesterification reaction is reversible, excess alcohol is required to shift the reaction towards ester production; thus, unreacted alcohol along with catalyst and glycerol need to be separated/recovered at the end of reaction. Also, the presence of free fatty acids in the feedstock leads to saponification, which results in the loss of catalyst and a decrease in the yield of esters [16]. Finally, while biodiesel is compatible with petro diesel, it exhibits a relatively high melting point (which limits its usage in cold climate regions) and lower oxidative stability compared to diesel [4,8,17,18]. As a result, use of biodiesel as a fuel is somewhat restricted since it is not considered as a “drop-in” alternative to hydrocarbon fuels and does not meet the ASTM D975 specification in the United States and EN 590 in Europe.

As an alternative, pyrolysis (or thermal cracking in the absence of  $O_2$ ) of vegetable oil can produce hydrocarbons that are compatible with a variety of petro-fuels such as gasoline, jet and diesel [19–22]. Studies on pyrolysis of seed oils, such as canola, palm, and soybean reveal that the primary compounds in the product are paraffins, olefins, carboxylic acids, and small amounts of aromatics [23–27]. Although a mixture is produced, the pyrolysis products can be separated (e.g. using distillation) and used either directly or processed by common refinery methods such as hydrogenation, hydrotreatment or alkylation to obtain gasoline and/or diesel like fuels. Further, unlike transesterification, conversion of triglycerides by pyrolysis avoids the use of methanol and unrecoverable homogenous catalysts. In addition, the un-degraded long-chain fatty acids from pyrolysis (e.g. oleic acid) can be separated from hydrocarbons to serve as feedstock for oleochemical production [28,29].

Pyrolysis of vegetable oils has typically been carried out in batch reactors at a temperature range of 300–500 °C and atmospheric pressure [9,30]. However, batch processes are not appropriate for commodity scale industrial operations due to low throughput. In addition, most batch studies report low yield of liquid products, likely due to the high residence time in these closed systems which allows secondary reactions of primary products to low molecular weight ( $C_1$ – $C_4$ ) noncondensable gases. For example, Chang and Wan [31] performed batch pyrolysis of tung oil at 450 °C and residence time of 100 min and reported only 55% yield of liquid products. More recently, Kubatova et al. [32] conducted batch pyrolysis of canola and soybean oil at 440 °C but at a lower residence time of 10 min and also with high hydrogen pressure (2200 kPa). This approach resulted in higher organic liquid product (OLP) yields (67% OLP for soybean oil and 61–69% for canola oil) likely due to the shorter reaction time and in situ hydrogenation of unsaturated primary products that lowered the production of secondary noncondensable gases.

In an effort to develop a continuous process for vegetable oil pyrolysis, Idem et al. [27] performed thermal cracking of canola oil. Their reactor consisted of a fixed-bed of inert materials (ceramic and quartz glass chips) that was kept at 500 °C. Due to the high reactor temperature and surface area created by inert particles, feed likely vaporized and cracked simultaneously. However, the residence time was still high (18 min) and only 15% of feed was recovered as OLP in their experiments. Nearly 75% of feed was lost as uncondensed gases such as small chain hydrocarbons ( $C_1$ – $C_4$ ) and  $H_2$ .

Akin to the concepts of fast pyrolysis of solid substrates (e.g. biomass and coal), which are carried out at high temperature and short residence time to maximize liquid products [33–35], OLP yields from vegetable oils are expected to be better in continuous reactors with low residence time, since secondary reactions would be minimized due to continuous product removal and condensation. Theoretical reaction mechanisms proposed by Maher et al.

[9] also suggest that liquid formation would be more favorable at low residence time. In recent times, Meier and co-workers have explored this approach in a series of studies and have reported improved liquid product yields [36–38]. For instance, continuous pyrolysis of waste fish oil during these studies resulted in the relatively high yield of 72% liquid products at reaction temperature of 525 °C and low vapor residence time of 24 s [36,37]. In addition to short residence time, a high free fatty acid content in the feed also possibly contributed to the high yields of OLP since fatty acids are more amendable to thermal cracking than triglycerides [23]. While yields were improved, nearly 30% of feed material was still lost to uncondensed gases. An additional drawback of the reaction system proposed by Meier and co-workers is the requirement of preheating the feed. Since the objective was to quickly vaporize the feed in the reactor (for short residence time), the feed was preheated to 475 °C. Thus, while the pyrolysis residence time was short, the overall time period for which feed was exposed to high temperature was still large and could have possibly resulted in some oil degradation during preheating. Including a preheater would also increase the capital cost of the reaction system.

From these studies reported in the literature, it can be noted that liquid product yields were typically in the range of 20–70% depending on reaction conditions, feedstock and reactor design. Liquid products, rather than gas are more desirable, since they have higher heating values on a volumetric basis and are easy to store and transport. Although pyrolysis of vegetable oil is more desirable than transesterification since it allows the direct production of hydrocarbons fuels, *pyrolysis technology has not yet attracted commercial interest due to the key bottleneck of the inability to achieve high liquid yields*. The goal of this study was to improve the yield of liquid products during pyrolysis. As such, conversion of soybean oil was carried out in a novel continuous pyrolysis system equipped with an atomizer. This allowed introduction of micron-sized droplets of oil that could be rapidly vaporized inside the pyrolysis tube. With this design, we were able to achieve low vapor residence times without preheating the feed. Since atomization is frequently utilized in car engines, painting/coating industries, and pharmaceutical manufacturing processes, it is expected that this common approach could be easily implemented on industrial scale. The influence of temperature and vapor residence time on conversion, product yields and composition of soybean oil pyrolysis was investigated.

## 2. Experimental

### 2.1. Materials

Soybean oil was obtained from Zoyeoil (Zeeland, MI, USA). Hexane, chloroform, methanol, *N*-methyl-2-pyrrolidone (NMP), sulfuric acid and enriched oleic acid were purchased from Fisher Scientific (Pittsburgh, PA, USA). Analytical standards for fatty acids (stearic acid, oleic acid, linoleic acid, and palmitic acid), glycerides (triolein, diolein, and monoolein), FAMES (mixtures of  $C_8$ – $C_{22}$  FAMES), alkanes ( $C_5$ ,  $C_6$ ,  $C_7$ ,  $C_8$  and mixtures of  $C_7$ – $C_{30}$ ), olefins-(Alphagaz PIANO), and aromatics-(Alphagaz PIANO) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

### 2.2. Experimental set-up

All experiments were performed in a continuous pyrolysis system that is schematically shown in Fig. 1. A stainless steel tube with an inner diameter (ID) of 2.18 cm and length of 23 cm served as the pyrolysis reactor. The tube was placed in a clam-shell furnace (Applied Test Systems, Butler, PA, USA) with 10 cm ID and 38 cm length and equipped with a temperature controller to main-

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