



Research Paper

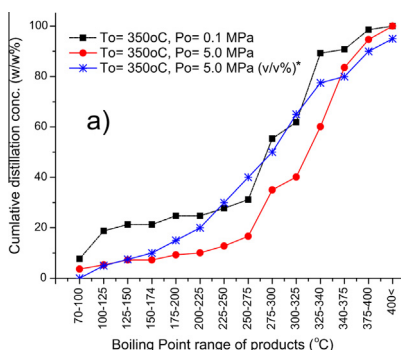
Study of non-catalytic thermal decomposition of triglyceride at hydroprocessing condition

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HIGHLIGHTS

- Thermolysis of triglycerides occurs above 300 °C and cracking intensify above 350 °C.
- Decomposition of carboxylic group observed, and β-H abstraction gives radical.
- Product contains aldehyde, ketonic, saturated/unsaturated, cyclic, glycerol group.
- Gasoline fraction contains lighter, cyclic and unsaturated hydrocarbons.
- Residues contain ester, dimer and carboxylic groups.

GRAPHICAL ABSTRACT



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ABSTRACT

Non-catalytic thermal decomposition of triglyceride is studied between 300 and 410 °C at 0.1 and 5 MPa in the presence of H₂ or inert gas. This test is carried in tubular reactor filled with inert material (borosilicate glass pellet). The qualitative and analytical results showed that *n*-alkanes and alkenes with oxygenated olefins were primary products, consistent with thermal cracking to lighter hydrocarbons. The resulting outlet fuel gas obtained mainly from the radical reaction and had high concentration of CO, ethylene and methane. The decomposition forms a large number of radical compounds containing acids, aldehydes, ketones, aliphatic and aromatic hydrocarbon groups. Lighter fraction contains mostly naphthenic group, and heavy fraction contains straight chain paraffinic hydrocarbons. When H₂ partial pressure raised, the cracking of heavy fractions is low, and products contain low concentration of the lighter and gasoline fractions. Here, the thermal decomposition of triglyceride yields lighter fractions due to cracking, decarboxylation and decarbonylation.

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Abbreviations: DCA, decarbonylation; DCO, decarboxylation; HDO, hydro deoxygenation; OLP, organic liquid product; OGP, organic gaseous product; GC, gas chromatography; FID, flame ionization detector; TCD, thermal conductivity detector; FT-IR, Fourier Transform Infrared Spectroscopy; BP, boiling point; CO, carbon monoxide; -(C=O), aldehyde or ketone group; C_x, hydrocarbon chain with x number of methyl group; O(OC), carboxylic radicals.

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1. Introduction

Renewable fuels is consider as a main alternative for overreliance of conventional diesel [1]. Esterification, pyrolysis, catalytic cracking, catalytic hydro-treatment and hydrothermal are various processes to produce renewable fuels from vegetable oils/animal fats [2–8]. In some cases, blending vegetable oil with conventional

fuels can be practised and used for combustion engine [3–6]. The biomass techno-economic assessment reveal that renewable fuels production has the barrier in capital investment, logistics and resource selection [9,10]. Presently, catalytic hydroprocessing of conventional diesel blended with vegetable oil or Fatty acid methyl ester (FAME) established in producing low sulphur (<10 ppmw) fuel-grade diesel in refineries [11,12]. This blend with vegetable oil (diesel:vegetable oil = 70:30) were investigated at 350–450 °C, 40–150 bar and liquid hourly space velocities of 0.5–5 h⁻¹ on sulphide Ni or Co–Mo/Al₂O₃ catalysts. Also, the processes yield CO_x (CO and CO₂) as undesired by-product by decarboxylation (DCO)/decarbonylation (DCA) reaction pathway [10,12–14]. Here, shorter residence time (flow reactor) of feed to catalyst results in 2–4% CO_x whereas longer residence time (batch reactor) results 10–15% CO_x [13,14]. Pyrolysis (cracking above 450 °C) produces lighter hydrocarbons such as alkanes and alkenes with 20% CO_x, this process a viable alternative for catalytic hydroprocessing [7,15]. The ester ~H₂C–O–(CO)CH₂~ bond breaking from triglyceride or FAME (DCA and DCO) brought by thermal decomposition (thermolysis), result in oxygenate (aldehyde or kenotic group form of paraffinic straight chain hydrocarbon radicals) compounds [12–14].

Generally, thermal decomposition depends on the reactor temperature and its internal surface area which possess different issues; for instance, a substantially higher ratio of internal tube surface to the reaction volume, and thus creates with internally different axial and radical temperatures at relative to the flow rate of feed [16]. Thus, the study of decomposition within moderate operating temperature has direct effect at internal surface of reactor. The axial temperature effect in axial flow direction creates radicals from the triglycerides ester [17]. Considering redox and thermal conductivity properties, radicals formed by cracking will disappear faster within molecular or atomic transfers. Bakhshi et al. observed canola oil cracking into low and middle distillate organic liquid product (OLP) at 400–500 °C. The observed total canola oil conversion was 93.9% for 370 °C and space velocity of 3.3 h⁻¹ in atmospheric pressure [18]. Hydro-deoxygenating (HDO) triglyceride to paraffinic straight chain hydrocarbon by removal of water and propane is favoured on about 300–370 °C with elevated pressure [19,20]. Also, this temperature reasoned in loss of one carbon from triglyceride esters (such as CO or CO₂) through DCA/DCO mechanism, which also reduces cetane value of the OLP [19].

The thermal effect at vegetable oil triglycerides during hydroprocessing has studied on catalyst surface. Metal surface and inert material in hydroprocessing system has to consider for thermal cracking. Catalytic hydroprocessing system consists of pre-heater followed to catalytic reactor and purification section. Here, pre-heater act as heat exchanger, and monitor reactor feed at specified hydroprocessing condition such as temperature, flow rate and pressure. Large industrial pre-heater's wall surface area to the feed volume has to consider for monitor the cracking during HDO mechanism. The thermolyses obviously influence by temperature but effect of residence time and H₂ partial pressure in the reactor should be consider as well. In general, the literature survey shows that specific catalytic hydroprocessing condition ranges between 250 and 400 °C with partial pressure of 0.1–5 MPa. Thermolysis at moderate temperature (represents catalytic hydroprocessing condition) ranges from 300 to 400 °C had not investigated to identify the triglyceride dissociation. This dissociation results in cracking into radicals from ester compound by two bond breaking mechanism such as breaking between glycerides (from propyl) carbon to ester oxygen ~H₂C–O(C=O)~ and ester oxygen to carbonyl straight chain hydrocarbon ~H₂C–O–(C=O)R (where R = (CH₂)₁₆CH₃). Hydrocarbons produced by thermal cracking of vegetable oil without use of H₂ partial pressure from previous research had incorporated in hydroprocessing system for

understanding temperature effect on inert material. The study on thermal decomposition of ester in absence of catalyst over triglyceride or FAME had focused. Also, the studies have investigated the stability in OLP radicals from ester dissociation.

In this research study, the thermolysis of rapeseed oil over inert material such as quartz was evaluated by allowing feed oil at 22.5 ml/h and in moderate condition (between 300 and 410 °C and 0.1 & 5.0 MPa). The result enables to understand the thermal effect on any vegetable oil or FAME, and also to observe the radical reaction from triglyceride dissociation.

2. Experiment

2.1. Feed and chemicals

The refined rapeseed oil (without free fatty acids) was purchased in the retail market, which contained triglycerides in the form of 7% stearic acid (18:0), 61.1% oleic acid (18:1) and 20.9% linoleum acid (18:2); the rest (i.e. 11%) consisted of omega-3 (shown in Table 1). The FAME type compounds: Dodecanoic acid (>98% from Sigma Aldrich) and Methyl oleate (>98% from Sigma Aldrich) in hexadecane (>98% from TCI Europe) were used as feed. The butyl benzene (>99% purity from Sigma Aldrich) was used for internal standardization.

2.2. Reactor

The experimental set-up [12] consisted of a continuous tubular reactor, feed and product tank, gas flow-meter, pump and controllers, see set-up sketch in Fig. 1. The effect of variation of space velocity (ml/h), reaction pressure (P_o) (MPa) and reaction temperature (T_o) (°C) on OLP yield was studied. The tubular reactor (31 ml inner liquid volume), vertical height 619.4 mm and filled with 2 mm diameter spherical boron silicate glass pellets, had electric furnace that was connected with a controller to regulate temperature and flow meter to regulate pressure. Both inlet and outlet of the reactor were fastened with heavy bolts (thickness of 19.3 mm), which was connecting the inlet and outlet pipes. The reaction temperature is monitored through PID controllers with three temperatures (T1, T2 and T3) placed in the reactor. Organic liquid product (OLP) was collected under ambient atmospheric conditions manually at the bottom of the product tank, and OLP was analyzed using Varian gas chromatography (GC). Organic gaseous products (OGP) was analyzed directly by online gas chromatography.

2.3. Analytical study

Simulated distillation (ASTM D2887) was performed in gas chromatograph (GC) technique (Varian 3400) equipped with a packed column (10% silicon OV-101, 80–100 mesh, 1 m × 1/8" × 2.00 mm) and a flame ionization detector (FID). Sam-

Table 1
Analysis of C, H & O elements of refined rapeseed oil feedstock.

Fatty acid content	Mol. form.	wt%	C (wt%)	H (wt%)	O (wt%)
Free Fatty Acids (FFA)		0	0	0	0
Stearic (18:0)	C ₁₈ H ₃₆ O ₂	7	5.4	0.9	0.8
Oleic (18:1)	C ₁₈ H ₃₄ O ₂	61.1	46.9	7.4	7.0
Linoleic (18:2)	C ₁₈ H ₃₂ O ₂	20.9	16.1	2.2	2.4
Linolenic (18:3)	C ₁₈ H ₃₀ O ₂	9.1	7.0	0.9	1.0
Gadoleic (20:1)	C ₂₀ H ₃₀ O ₂	1.4	1.2	0.1	0.2
Erucic (22:1)	C ₂₂ H ₃₂ O ₂	0.5	0.5	0.1	0.1
Total calculated (wt%)		100	77.0	11.6	11.4
Analysed* (wt%)	Error = ±0.5%	100	77.1	11.8	11.1

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