Video Article

Laboratory Production of Biofuels and Biochemicals from a Rapeseed Oil through Catalytic Cracking Conversion

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Abstract

The work is based on a reported study which investigates the processability of canola oil (bio-feed) in the presence of bitumen-derived heavy gas oil (HGO) for production of transportation fuels through a fluid catalytic cracking (FCC) route. Cracking experiments are performed with a fully automated reaction unit at a fixed weight hourly space velocity (WHSV) of 8 hr^{-1}, 490-530 °C, and catalyst/oil ratios of 4-12 g/g. When a feed is in contact with catalyst in the fluid-bed reactor, cracking takes place generating gaseous, liquid, and solid products. The vapor produced is condensed and collected in a liquid receiver at -15 °C. The non-condensable effluent is first directed to a vessel and is sent, after homogenization, to an on-line gas chromatograph (GC) for refinery gas analysis. The coke deposited on the catalyst is determined *in situ* by burning the spent catalyst in air at high temperatures. Levels of CO_2 are measured quantitatively *via* an infrared (IR) cell, and are converted to coke yield. Liquid samples in the receivers are analyzed by GC for simulated distillation to determine the amounts in different boiling ranges, *i.e.*, IBP-221 °C (gasoline), 221-343 °C (light cycle oil), and 343 °C+ (heavy cycle oil). Cracking of a feed containing canola oil generates water, which appears at the bottom of a liquid receiver and on its inner wall. Recovery of water on the wall is achieved through washing with methanol followed by Karl Fischer titration for water content. Basic results reported include conversion (the portion of the feed converted to gas and liquid product with a boiling point below 221 °C, coke, and water, if present) and yields of dry gas (H_2-C_2's, CO, and CO_2), liquefied petroleum gas (C_3-C_4), gasoline, light cycle oil, heavy cycle oil, coke, and water, if present.

Video Link

The video component of this article can be found at http://www.jove.com/video/54390/

Introduction

There is strong global interest in both the private and public sectors to find efficient and economic means to produce transportation fuels from biomass-derived feedstocks. This interest is driven by a general concern over the substantial contribution of burning petroleum fossil fuels to greenhouse gas (GHG) emissions and its associated contribution to global warming. Also, there is strong political will in North America and Europe to displace foreign-produced petroleum with renewable domestic liquid fuels. In 2008, biofuels provided 1.8% of the world's transportation fuels[1]. In many developed countries, it is required that biofuels replace from 6% to 10% of petroleum fuels in the near future[2]. In Canada, regulations require an average renewable fuel content of 5% in gasoline starting December 15, 2010[3]. The Renewable Energy Directive (RED) in Europe has also mandated a 10% renewable energy target for the European Union transport sector by 2020[4].

The challenge has been to develop and demonstrate a viable economic pathway to produce fungible transportation fuels from biomass. Biological sources include triglyceride-based biomass such as vegetable oils and animal fats, as well as waste cooking oil and cellulosic biomass such as wood chips, forest wastes, and agriculture residues. Over the past two decades, research has focused on the evaluation of biomass-derived oil processing using conventional fluid catalytic cracking (FCC)[5-12], a technology responsible for producing most of the gasoline in a petroleum refinery. Our novel approach in this study is to co-process canola oil mixed with oil sands bitumen-derived feedstock. Normally, bitumen must be upgraded prior to refining, producing refinery feedstocks such as synthetic crude oil (SCO)—this processing route is particularly energy intensive, accounting for 68-78% of the GHG emissions from the SCO production[13] and, in 2011, constituting 2.6% of Canada's total GHG emissions[14]. Replacing a portion of upgraded HGO with biofeed would reduce GHG emissions, since biofuel production involves a much smaller carbon footprint. Canola oil is chosen in this work because it is abundant in Canada and the US. This feedstock possesses a density and viscosity similar to those of HGOs while the contents of sulfur, nitrogen, and metals that could affect FCC performance or product quality are negligible. Moreover, this co-processing option offers significant technological and economic advantages as it would allow utilization of the existing refinery infrastructure and, hence, would require little additional hardware or modification of the refinery. In addition, there may be potential synergy that could result in product quality improvement when co-processing a highly aromatic bitumen feed with its straight-chain biomass counterpart. However, co-processing involves important technical challenges. These include the unique physical and chemical characteristics of bio-feeds: high oxygen content, paraffinic-rich composition, compatibility with petroleum feedstocks, fouling potential, *etc.*

This study provides a detailed protocol for the production of biofuels at laboratory scale from canola oil through catalytic cracking. A fully automated reaction system – referred to in this work as the laboratory test unit (LTU)[15] – is used for this work. **Figure 1** shows schematically how this unit operates. This LTU has become the industry standard for laboratory FCC studies. The objective of this study is to test the suitability of the LTU for cracking canola oil to produce fuels and chemicals with the goal of mitigating GHG emissions.
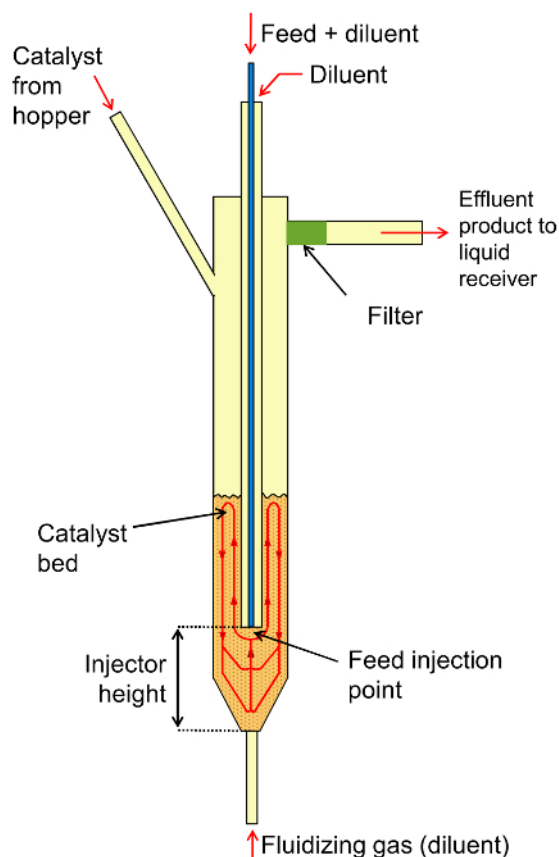

Figure 1: Conceptual illustration of the reactor. Illustration showing flow lines of the catalyst, feed, product, and diluent. Please click here to view a larger version of this figure.

Protocol

Caution: Please consult all relevant material safety data sheets (MSDS) before using the materials. Work with crude oil samples should only be done while wearing proper personal protective equipment (safety glasses, gloves, pants, closed-toe shoes, lab coat), and the opening, transfer and handling of crude samples should occur in a vented fumehood. Heated hydrocarbons can be flammable in air, and the reaction system should be carefully leak-checked prior to use with crude oil mixtures. The reactor can reach temperatures as high as 750 °C, and high-temperature safety gloves should be used when working near hot surfaces.

1. General Considerations

1. To make the best use of the automated reaction unit, which can complete six consecutive runs over ~8 hr, choose a constant feed rate of 1.2 g/min. This sets the weight hourly space velocity (WHSV) to 8 hr^{-1} through the relationship WHSV=60/[(C/O)×t]=60×(O/t)/C where t is the feed delivery time in minutes and C and O are masses of catalyst and feed, respectively, in grams. By changing the feed injection time, a set of catalyst/oil mass ratios of 4, 6, 8, 10, and 11.25 (x2) was attained for each reaction temperature in order to achieve a wide range of conversion.

2. Feedstock and Catalyst Preparation

1. Obtain an HGO by distilling off the -343 °C fraction (by spinning band) of a synthetic crude oil (SCO).
2. Purchase edible-grade canola oil from a local food store, and use without further treatment.
3. Prepare a 15 v% canola blend by mixing 79.645 g of HGO (0.9370 g/ml density) with 13.7535 g canola oil (0.9169 g/ml density).
4. Screen the equilibrium catalyst using a 60 Tyler mesh sieve (250 µm opening), followed by a second screening with a 400 Tyler mesh sieve (38 µm opening).
5. Calcine the on-size particles (38-250 µm) at 600 °C for 4 hr, then load them into the six hoppers of the automated reaction unit.

3. Test Procedure

1. System Preparation
    1. Program Preparation
        1. Using the software that controls the reaction unit, open the window for run conditions.
        2. Type in the identifications of the feed and catalyst, the barometric pressure, the injection time, and the temperature set points for the feed system, the reactor, the product line, the coolant, and the CO catalytic converter in each step of the run period.

    2. Catalyst Preparation
        1. For each catalyst glass hopper above the process tubing, remove the lid and charge 9 g of calcined on-size catalyst into the hopper. Attach an O-ring to the top of the hopper and re-clamp its lid.

    3. Calibration of Feed Rate
        1. Set the oil feed pump to deliver feed at a constant feed injection rate (1.2 g/min) for all the cracking runs.
        2. Disconnect the oil feed line below the purge valve (KV-114)[16] and attach a short temporary tube to the bottom of the valve for oil delivery into a tared beaker.
        3. Preheat the feedstock to 85 °C to enable the HGO-blend to flow easily in and out of the syringe and along the feed line.
        4. Set the injection time for calibrating the pump to the same value as that for the first run in the series (default setting).
        5. Tare a beaker, and place it at the discharge of the short temporary tubing. Start the preset "PUMPCAL" user program[17] in the reaction unit software.
        6. After the PUMPCAL program is complete, remove and weigh the beaker containing the feed. Divide the mass of feed delivered into the beaker by the injection time to obtain the feed rate.
        7. Adjust the pump speed to higher or lower (using the three-digit dial on the pump) and repeat steps 3.1.3.5 to 3.1.3.6 until the desired feed rate is attained.
        8. Remove the short temporary tube and re-connect the feed line.

    4. Calibration of GC for Gas Analysis
       Note: This step is necessary if the GC for gas analysis is found to be out of calibration, which can be inferred from reference checks, data trending, and material balance. Experience indicates that the GC calibration can be relied on for an extended period.
        1. Connect a cylinder of commercial multicomponent refinery gas standard to the hand valve (HV-190)[16].
        2. Load a method in the GC software that is capable of eluting and separating all the peaks in the refinery gas standard. Use the parameters for the GC method in **Table 1**.
        3. Using the GC software, perform an analysis run of the refinery gas standard.
        4. Open the chromatogram of the refinery gas standard and integrate the peaks in the chromatogram.
        5. Identify the peaks in the chromatogram, ensuring that all of the components in the calibration gas are found. Delete any peaks that are present but cannot be attributed to the components in the standard.
        6. Based on retention time ranges, lump and divide compounds eluting after C_5 into C_{6+1}, C_{6+2}, C_{6+3}, and C_{6+4} groups. For this method, lump pentene isomers into one C_5 olefin group.
        7. Using the GC software, assign concentration values to each integrated peak from the gas standard, under the Calibration function.
        8. Save the calibration into the method file, for use to determine the concentrations of peaks in subsequent test runs. Disconnect the commercial gas standard.

    5. Calibration of CO_2 Analyzer
        1. Through the reaction unit software, switch the valve (KV-170)[16] to the position that enables the zero gas (nitrogen) to flow to the IR gas analyzer. Adjust the flow by turning the knob in association with the flow control valve (FCV-107)[16], if necessary, to get about 250 sccm on the flow indicator (FI-107)[16].
        2. Zero the analyzer using the Zero adjustment screw on the front panel of the analyzer with the help of a flat-bladed screwdriver.
        3. Switch the hand valve (HV-107)[16] to supply the CO_2 (19.8 mole%) standard gas to the analyzer. Adjust the manual valve (MV-107)[16] to obtain a flow of approximately 250 sccm on the flow indicator (FI-107).
        4. Adjust the analyzer reading to match the concentration (19.8 mole%) of the standard span gas using the SPAN screw on the front panel.
        5. Disconnect the span gas and return the hand valve (HV-107) to the RUN position.

    6. Preparation of Liquid Product Receiver
       Note: Each receiver consists of a condenser and a GC vial connected to the bottom of the condenser by a short piece of silicone tubing.
        1. Sequentially assign numbers to the condensers and GC vials.
        2. Place a small plug of glass wool inside the top of each receiver outlet arm as shown in **Figure 2**.
        3. Keep the receiver upright with some support in a beaker or a flask of suitable size. Weigh each receiver in an analytical balance the top window of which is covered by a cubic plastic shield to ensure a draft-free environment (**Figure 3**).
        4. Record the dry mass (W_{before}) of the prepared receiver together with labeled stoppers.
        5. Install and connect the weighed receiver to the product line (**Figure 4**).

    7. Reactor Preparation
        1. Install an oil feed line in the reactor with a length that allows for a 1.125 inch injector height.
        2. Place a filter at the exit of the reactor to prevent any catalyst dust from entering the product line, changing the filter after 50-100 runs.
        3. Perform a pressure test on the reactor system by running the program PTEST1[17] after feed pump calibration and installation of the receivers. Close the gas vent and pressurize the reactor system with 150 mmHg nitrogen, followed by isolation of the system.

4. Observe the pressure reading for a few minutes to ensure the pressure drop is no more than 0.4 mmHg per min indicating that no leaks are present. If a pressure drop of greater than 0.4 mmHg per min is observed, perform a leak test according to the manufacturer's instructions, and remedy any leaks accordingly.

Sample inlet T	90 °C	Post run pressure	30 psi	
Injector T	90 °C	Pressure equilibration	10 sec	
Run time	300 sec	Detectors	Thermal Conductivity	
Column pressure	30 psi	Data acquisition rate	50 Hz	
	Channel A	**Channel B**	**Channel C**	**Channel D**
Pre-column	PLOT-U; 30 μm × 320 μm × 3 m	PLOT-Q; 10 μm × 320 μm × 1 m	Alumina; 3 μm × 320 μm × 1 m	-
Column	Molsieve; 12 μm × 320 μm × 10 m	PLOT-U; 30 μm × 320 μm × 8 m	Alumina; 8 μm × 320 μm × 10 m	OV1; 2 μm × 150 μm × 10 m
Carrier gas	Argon	Helium	Helium	Helium
Inlet mode	Backflush	Backflush	Backflush	Fixed Volume
Column T	100 °C	90 °C	130 °C	90 °C
Injection time	30 msec	120 msec	0 msec	100 msec
Backflush time	12.5 sec	5.0 sec	5.5 sec	-

Table 1: GC method parameters for analysis of gas produced by the LTU.

Figure 2: Vial attachment to condenser. Photo showing the location of the glass wool plug and the attachment of a GC vial to the condenser with silicone tubing. Please click here to view a larger version of this figure.
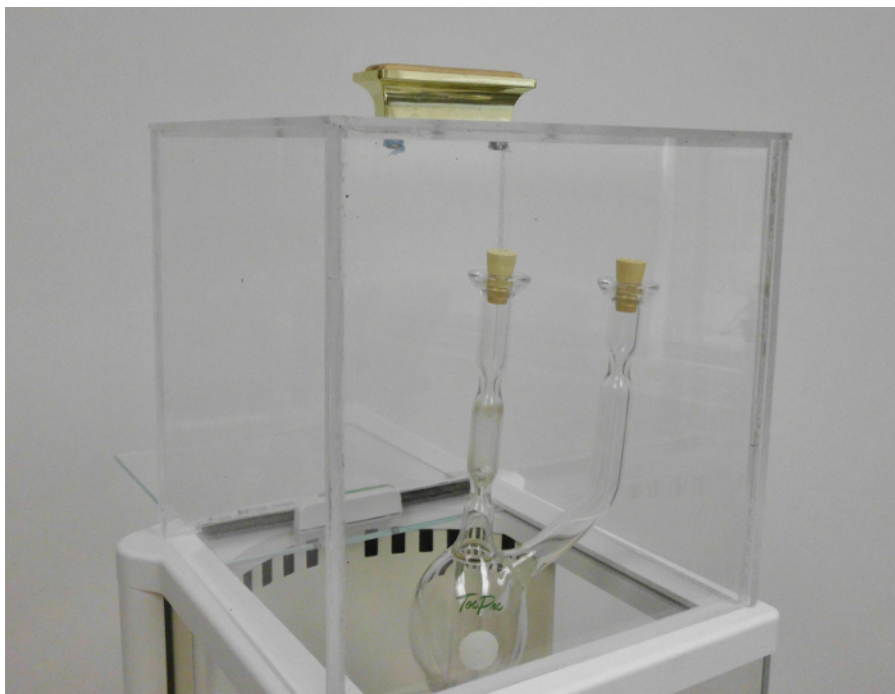
Figure 3: Weighing of product receiver. Plastic cover for the balance to weigh the long liquid product receiver, which may stick out of the top window. Please click here to view a larger version of this figure.

Figure 4: Liquid receiver attachment. Photo showing the attachment of liquid receivers to the product line. Please click here to view a larger version of this figure.

2. System Operation in Auto Mode
    1. On the LTU SETUP screen, input the relevant information for the experiment: run number, feed name, catalyst identification, atmospheric pressure, set points for skin and internal reactor temperatures for both cracking and catalyst regeneration, and oil injection time. Omit this step if full information has been included in Section 3.1.1.
    2. Place the system into run mode by clicking the "RUN" button on the process flow screen. This initiates the test sequence[17], which includes the steps in auto mode to be described in the Discussion.

3. Non-Auto Mode System Operation

   1. Using the computer attached to the GC, integrate the peaks and process the data using the calibration established. Input the final GC data into the LTU program through the LTU computer.

4. Post-run Operation
   1. Mass Determination of Liquid Product
      1. After removing the clamp, tilt the receiver and collect any liquid product droplets on the beveled metal tip below the product valve.
      2. Immediately seal the receiver with labeled rubber stoppers and carefully remove it from the bath. Rinse off the ethylene glycol from the bath with cold water and dry the outside with paper towel.
      3. Place the liquid product receiver on a rack at room temperature for 20 min, allowing any frozen product to thaw and run down into the GC vial at the bottom of the receiver.
      4. Collect the liquid holdup around the metal joint for the receiver with a tared cotton wool swab. Determine the mass of the liquid holdup (W_{swab}) and record.
      5. Open the liquid product receiver to atmosphere in a vented fume hood for pressure equalization by momentarily removing the stopper on the top outlet of the receiver.
      6. Put the stopper back on and obtain the receiver mass (W_{after}). Remove the GC vial from the condenser. Cap and store the product sample in a refrigerator at 4 °C for later analysis.
      7. If a water droplet appears at the GC vial bottom as in the case of cracking canola oil, use a clean syringe to transfer as much water-free oil product to another vial as possible and cap it immediately.
      8. Rinse the inner walls of the receiver condenser thoroughly with a small quality of methanol and collect all of the methanol wash into the original GC vial containing the water droplet. Cap the vial and obtain the mass of the liquid inside for use in water determination.

   2. Analysis of Liquid Product for Simulated Distillation
      1. Using standard test method ASTM D2887[18], determine the mass percentage of the water-free liquid product boiling in the ranges of gasoline (IBP-221 °C), light cycle oil (LCO, 221-343 °C), and heavy cycle oil (HCO, 343 °C-FBP).

   3. **Analysis of Water Product**
      1. Using standard test method ASTM D4377[19], determine the water content (W_{H2O}) of the methanol wash combined with the water droplet in the vial.

5. Calculations
   1. Mass of Gaseous Product
      1. Calculate the total volume of gaseous product through the volume of water displaced according to the formula:

$$V_{gas} = V_{water} \times \frac{273}{273 + T} \times \frac{P}{101.3}$$

      where V_{gas} is volume (ml) of gas collected at standard conditions (0 K and 101.3 kPa), V_{water} is volume (ml) of water displaced during the test, T is gas temperature (°C) and P is gas pressure (kPa).
      2. Calculate the mass of each gas component using:

$$W_i = \frac{N_i V_{gas}/100 \times M_i}{22412}$$

      where W_i is mass (g) of the ith gaseous product, N_i is mol% of the ith component in the gas, and M_i is molecular weight of the ith gaseous product. The molecular weight of the C_5+ unresolved lump is assumed to be 86.
      3. Calculate the total mass of gaseous product as:

$$W_{gas} = \sum W_i$$

      where W_{gas} is the total mass of gaseous product, and W_i is the mass of the ith gaseous product as calculated in 3.5.1.2.

   2. Mass of Liquid Product
      1. Calculate the total mass of liquid product with:

      $W_{liq} = W_{after} - W_{before} + W_{swab}$

      where W_{liq} is mass (g) of the liquid product, W_{after} is mass (g) of the liquid product receiver after reaction, W_{before} is mass (g) of the liquid product receiver before reaction, and W_{swab} is mass (g) of the liquid holdup collected on the cotton swab.

   3. Mass of Coke
      1. Calculate the total mass of coke derived from the LTU using:

      $W_{coke} = W_{carbon} \times 1.0695$

      where W_{coke} is mass (g) of coke, W_{carbon} is mass (g) of carbon, and 1.0695 is the carbon-to-coke factor.

   4. Mass Balance (Recovery)

1. Calculate the mass balance using

$$R = (W_{gas} + W_{liq} + W_{coke}) \div W_{feed} \times 100$$

where R is recovery (mass% of feed) and W_{feed} is mass (g) of the oil feed. R should be in the range of 96 to 102%. If not, reject the test as unsatisfactory.

5. Unnormalized Yields and Conversion
   Note: Calculate each product yield (mass% feed) according to the formulas given below.
   1. Calculate Dry Gas (H_2-C_2's, CO, and CO_2)

   $$Y_{DG} = (W_{H2} + W_{C1} + W_{C2} + W_{CO} + W_{CO2}) \div W_{feed} \times 100$$

   where Y_{DG} is unnormalized yield (mass% feed) of the dry gas, W_{H2} is mass (g) of H_2, W_{C1} is mass (g) of the C_1 gas (methane), W_{C2} is mass (g) of the C_2 gas (ethane and ethylene), W_{CO} is mass (g) of CO, and W_{CO2} is mass (g) of CO_2. Note that correction for the minute amount of CO_2 dissolved in water is not necessary.
   2. Calculate Liquefied Petroleum Gas (LPG)

   $$Y_{LPG} = (W_{C3} + W_{C4}) \div W_{feed} \times 100$$

   where Y_{LPG} is unnormalized yield (mass% feed) of the LPG product, W_{C3} is mass (g) of the C_3 gas (propane and propylene), and W_{C4} is mass (g) of the C_4 gas (butanes and butenes including 1,3-butadiene).
   3. Calculate Gasoline

   $$Y_{GLN} = [X_{GLN} \times (W_{liq} - W_{H2O} - W_{swab}) + W_{C5+}] \div W_{feed} \times 100$$

   where Y_{GLN} is unnormalized yield (mass% feed) of gasoline, X_{GLN} (obtained by simulated distillation) is mass fraction of gasoline in the water-free liquid product, W_{H2O} is mass (g) of water in the liquid product, if any, and W_{C5+} is mass (g) of C_5+ product in the gas phase (unresolved C_6 plus C_6+ lump).
   4. Calculate Light Cycle Oil (LCO)

   $$Y_{LCO} = [X_{LCO} \times (W_{liq} - W_{H2O} - W_{swab})] \div W_{feed} \times 100$$

   where Y_{LCO} is unnormalized yield (mass% of feed) of the LCO product and X_{LCO} (obtained by simulated distillation) is mass fraction of LCO in the water-free liquid product.
   5. Calculate Heavy Cycle Oil (HCO)

   $$Y_{HCO} = [X_{HCO} \times (W_{liq} - W_{H2O} - W_{swab}) + W_{swab}] \div W_{feed} \times 100$$

   where Y_{HCO} is unnormalized yield (mass% feed) of HCO and X_{HCO} (obtained by simulated distillation) is mass fraction of HCO in the water-free liquid product.
   6. Calculate Coke

   $$Y_{coke} = W_{coke} \div W_{feed} \times 100$$

   where Y_{coke} is unnormalized yield (mass% feed) of coke.
   7. Calculate Water

   $$Y_{H2O} = W_{H2O} \div W_{feed} \times 100$$

   where Y_{H2O} is unnormalized yield (mass% feed) of water.
   8. Calculate Conversion

   $$CON_{unnorm} = 100 - Y_{LCO} - Y_{HCO}$$

   where CON_{unnorm} is unnormalized conversion (mass% feed).

6. Normalized Yields and Conversion

$$Y^0_i = Y_i \div R \times 100$$

where Y^0_i is normalized yield (mass% feed) of the ith product.

$$CON_{norm} = 100 - Y^0_{LCO} - Y^0_{HCO}$$

where CON_{norm} is normalized conversion (mass% feed).

Representative Results

The established protocol has been successfully applied to an oil blend of 15:85 volume ratio (*i.e.*, 14.73:85.27 mass ratio) between canola oil and an SCO-derived HGO[20]. For practical reasons (cost, availability of canola oil, and possible challenges in commercial operation), the study was focused on feedstock containing 15 v% canola oil addition, although feeds with higher concentrations were also tried. The blend was catalytically cracked at 490-530 °C and 8.0 hr^{-1} WHSV with varying catalyst/oil ratios (in the sequence 11.25, 10, 8, 6, 4, and 11.25). For comparison, the base oil (pure HGO) was also cracked under the same conditions. **Table 2** gives the conversion and yield data which have been discussed in detail previously[20]. In cracking the blend, assuming there is no interference between the two components, the apparent yields contributed by each can be calculated arithmetically. **Table 2** demonstrates qualitatively that, upon cracking, the canola oil in the blend contributes substantially to the yields of biofuels (*e.g.*, gasoline and diesel) and biochemicals (*e.g.*, propane, propylene, i-butane, and butylenes in LPG). Following the above assumption, the negative calculated HCO yields contributed by canola oil (15 v% in the blend) in fact result from interference between the two components during cracking[20].

Actual Yields of Base Oil (HGO)																		
Temperature, °C	490						510						530					
Catalyst-to-Oil, g/g	4.02	6.00	8.04	10.00	11.25	11.25	4.02	6.00	8.04	10.00	11.25	11.25	4.02	6.00	8.04	10.00	11.25	11.25
Conversion, mass%	57.50	62.06	64.95	66.83	66.77	67.62	59.79	65.23	66.99	69.11	69.45	69.37	61.57	65.82	68.50	70.16	70.02	69.82
Recovery, mass%	99.72	99.35	99.17	99.27	99.12	100.10	99.3	99.9	99.2	99.2	99.2	99.95	99.63	99.66	99.38	99.54	98.48	98.38
Yields, mass %:																		
Dry Gas	1.28	1.49	1.65	1.71	1.80	1.79	1.73	1.92	2.07	2.17	2.26	2.24	2.33	2.60	2.76	2.90	3.00	2.99
LPG	10.96	12.33	13.39	13.80	13.42	14.06	12.54	13.83	14.45	15.10	15.13	15.10	14.01	15.43	16.27	16.90	16.98	17.14
Gasoline	42.00	44.00	44.67	45.09	44.71	45.10	42.06	44.97	44.95	45.34	44.85	45.07	41.64	42.75	43.45	43.33	43.15	42.76
LCO	21.86	20.65	19.72	19.23	19.30	18.79	20.53	19.09	18.62	18.01	17.62	17.79	19.39	18.24	17.50	16.79	16.75	16.94
HCO	20.64	17.29	15.33	13.94	13.93	13.59	19.68	15.68	14.39	12.89	12.93	12.85	19.03	15.94	14.00	13.04	13.23	13.23
Coke	3.27	4.24	5.23	6.22	6.84	6.67	3.47	4.51	5.53	6.49	7.21	6.96	3.59	5.04	6.03	7.04	6.90	6.92
H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Actual Yields of Blends (15 v% Canola Oil in HGO)																		
Temperature, °C	490						510						530					
Catalyst-to-Oil, g/g	4.02	6.00	8.04	10.00	11.25	11.25	4.02	6.00	8.04	10.00	11.25	11.25	4.02	6.00	8.04	10.00	11.25	11.25
Conversion, mass%	58.80	63.93	66.78	67.79	68.10	68.78	64.83	68.72	70.96	71.89	72.09	71.98	67.12	70.44	72.52	73.26	73.51	73.81
Recovery, mass%	98.78	99.46	99.12	99.13	99.76	99.53	99.41	99.18	99.27	99.21	99.29	100.07	99.20	99.44	99.23	99.89	99.10	99.19
Yields, mass %:																		
Dry Gas	1.47	1.68	1.86	1.92	2.04	2.00	1.96	2.18	2.32	2.41	2.55	2.53	2.54	2.77	2.94	3.04	3.35	3.21
LPG	11.39	12.70	13.77	14.37	14.33	14.61	13.48	14.90	15.71	16.12	15.96	16.36	15.05	16.35	17.10	17.53	17.59	18.13
Gasoline	40.64	42.78	43.40	42.73	42.61	42.99	43.58	44.63	45.01	44.55	44.21	43.77	43.46	44.07	44.17	43.46	42.95	42.70
LCO	21.81	20.31	19.44	19.09	19.25	18.74	19.05	17.84	17.04	16.76	16.71	16.87	17.95	16.77	16.03	15.77	15.62	15.63
HCO	19.38	15.76	13.78	13.11	12.65	12.48	16.12	13.44	11.99	11.35	11.20	11.14	14.93	12.79	11.45	10.97	10.86	10.56
Coke	3.41	4.68	5.57	6.66	6.99	6.94	3.75	4.77	5.68	6.59	7.10	7.02	4.02	5.11	6.04	6.92	7.46	7.51
H_2O	1.89	2.08	2.17	2.11	2.14	2.25	2.06	2.23	2.24	2.23	2.27	2.30	2.06	2.15	2.26	2.31	2.17	2.26
TOTAL	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Calculated Yields (mass%) Contributed by 85 v% (85.27 mass%) HGO in the Blend																		

Dry Gas	1.09	1.27	1.41	1.46	1.54	1.53	1.47	1.64	1.76	1.85	1.93	1.91	1.99	2.22	2.35	2.47	2.56	2.55
LPG	9.35	10.51	11.42	11.77	11.44	11.99	10.69	11.79	12.32	12.88	12.90	12.87	11.95	13.16	13.87	14.41	14.48	14.62
Gasoline	35.81	37.52	38.09	38.45	38.12	38.45	35.86	38.34	38.33	38.66	38.24	38.43	35.51	36.45	37.05	36.95	36.79	36.46
LCO	18.64	17.61	16.82	16.40	16.45	16.02	17.51	16.28	15.88	15.35	15.02	15.17	16.54	15.55	14.92	14.32	14.28	14.45
HCO	17.60	14.74	13.07	11.89	11.88	11.59	16.78	13.37	12.27	10.99	11.03	10.95	16.23	13.59	11.94	11.12	11.28	11.28
Coke	2.79	3.62	4.46	5.31	5.84	5.69	2.96	3.85	4.71	5.53	6.15	5.93	3.06	4.30	5.14	6.00	5.88	5.90
H_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27	85.27
Calculated Yields (mass%) Contributed by 15 v% (14.73 mass%) Canola Oil in the Blend																		
Dry Gas	0.39	0.41	0.46	0.46	0.50	0.47	0.49	0.55	0.56	0.56	0.62	0.62	0.55	0.55	0.59	0.57	0.80	0.66
LPG	2.05	2.19	2.36	2.60	2.89	2.61	2.79	3.11	3.39	3.24	3.06	3.49	3.10	3.19	3.23	3.13	3.11	3.52
Gasoline	4.82	5.26	5.31	4.28	4.49	4.54	7.72	6.29	6.68	5.88	5.97	5.34	7.95	7.61	7.12	6.51	6.16	6.23
LCO	3.17	2.70	2.62	2.69	2.80	2.72	1.55	1.56	1.17	1.41	1.69	1.71	1.41	1.21	1.11	1.45	1.34	1.19
HCO	1.78	1.01	0.71	1.23	0.77	0.89	-0.66	0.07	-0.28	0.36	0.17	0.19	-1.30	-0.80	-0.49	-0.16	-0.41	-0.73
Coke	0.63	1.07	1.11	1.35	1.15	1.26	0.79	0.92	0.97	1.05	0.95	1.09	0.96	0.81	0.90	0.92	1.57	1.61
H_2O	1.89	2.08	2.17	2.11	2.14	2.25	2.06	2.23	2.24	2.23	2.27	2.30	2.06	2.15	2.26	2.31	2.17	2.26
Total	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73	14.73
Recovery, mass%																		
Mean 99.35																		
Standard deviation 0.31																		

Table 2: FCC performances of the base oil and the blend and the apparent conversions and product yields of the components in the blend. Please click here to download this table as a Microsoft Excel spreadsheet.

The presence of water and CO plus CO_2 (included in dry gas) as cracked products from the blend but not from HGO alone (**Table 2**) is a direct indication that canola oil in the blend participates in reactions. Water is produced by combination of hydrogen and oxygen and CO and CO_2 are released from decarbonylation and decarboxylation of fatty acids in canola oil, respectively.

Other evidence of cracking of canola oil in the blend is presented in **Figure 5**, which shows the effect of process parameters on H_2 and CO yields. Observations demonstrate that all yields are not very sensitive to C/O ratio changes for a feed at a given temperature. However, for a feed at a given C/O ratio, both H_2 and CO yields increase with increasing temperature, which is the driving force for cracking (Note: No CO from HGO at any temperature). Comparing the two feeds, the blend gives higher CO yields but lower H_2 yields than the base oil at the same severity in terms of C/O ratio and temperature. The latter observation is attributable to water formation from hydrogen and oxygen during cracking of the blend.
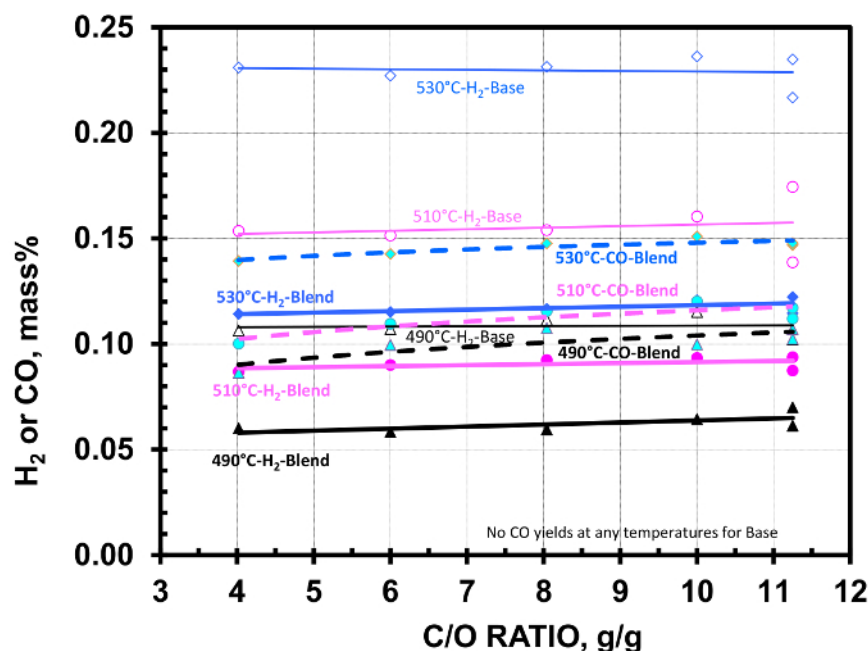
Figure 5: Variations of H₂ and CO yields with process parameters. Color code—black for 490 °C, pink for 510 °C, blue for 530 °C; thin solid lines—H₂ yield of base oil, thick solid lines—H₂ yield of blend; thick dotted lines—CO yield of blend; no CO detected for base oil (0 mass% CO yield of base oil at three temperatures). Please click here to view a larger version of this figure.

Another interesting observation with canola oil is illustrated in **Figure 6**, which shows the reactor temperature profiles during operation. Before injection of an oil, the reactor is at a nominal temperature of 530 °C. After injection, the reactor temperature drops (due to heating, vaporization, and cracking of the oil), reaching a minimum (heat consumption is in balance with heat input from the control system once the temperature drops to a certain limit) and rising towards the initial temperature. As such, one may use the minimum temperature as a measure of the heat required for the overall process. For a given feed, the minimum temperature depends on the amount of oil injected or the C/O ratio since the catalyst weight remains constant. As C/O ratio increases, the temperature drop decreases since less oil is injected. Comparing the two feeds, the blend consistently exhibits a smaller drop by about 1.5 °C at a given C/O ratio due to the heat release from the exothermic reaction H_2 (g) + ½ O_2 (g) → H_2O (g) (-241.8 kJ/mol at 25 °C)[21]. Similar phenomena are also observed at the other two reaction temperatures.
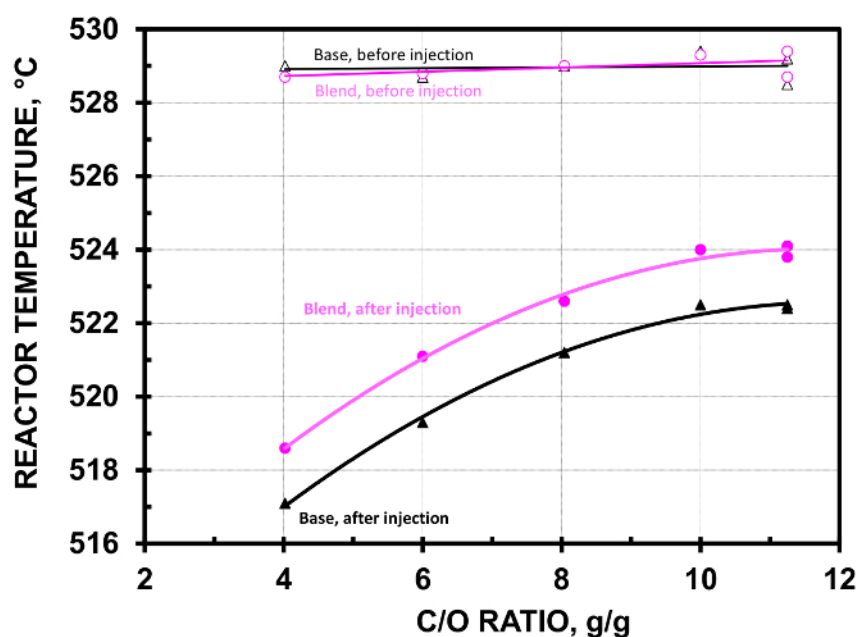

Figure 6: Reactor temperature drops before and after feed injection at 530 °C (nominal). Color code – black for base oil, pink for blend; thin lines – before feed injection; thick lines – after feed injection. Please click here to view a larger version of this figure.

Discussion

The protocol described here utilizes cyclic operation of a single reactor containing a batch of fluidized catalyst particles to simulate feed oil cracking and catalyst regeneration. The oil to be cracked is preheated and fed from the top through an injector tube with its tip close to the bottom of the fluid bed. The vapor generated after catalytic cracking is condensed and collected in a receiver, and the liquid product collected is subsequently analyzed for simulated distillation to determine yields of fractions in different boiling ranges. The noncondensable gaseous product is sent to an on-line gas chromatograph for analysis to determine yields of dry gas and liquefied petroleum gas. The volume of the gaseous product is measured by the water displacement method. After suitable catalyst stripping time, the deposited coke on the catalyst is determined *in situ* by burning the deactivated catalyst in air at high temperatures (typically over 700 °C). Levels of CO_2 are measured quantitatively via an IR cell and are converted to coke yield. Any water formed is recovered and determined by Karl Fischer titration. The total recovery (mass balance) of the feed should be in the range of 96 to 102% prior to normalization of each product yield.

One benefit to this procedure is the use of the automated sequence carried out by the LTU during the reaction process. After initiating the test sequence in step 3.2.2, the system begins with system priming during which the LTU uses the preset conditions programmed prior to the run. If there is spent catalyst remaining in the reactor from previous runs, it is discharged into the waste vessel, and fresh catalyst from the specified hopper is loaded into the reactor. The system then waits a sufficient length of time to allow the temperatures of the reactor, feed line, syringe, and feed bottle to stabilize within 5 °C of their set points. The syringe is then filled at a feed rate of 1.2 g/min for 20 sec (corresponding to two slop times), plus injection time, and the product line is purged with N_2. The system then waits again, until the reactor internal and skin temperatures are within 2 °C of their set points, and the coolant temperature is within 3 °C of its set point. Finally, N_2 flow to the IR gas analyzer is started and the system records the initial mass on the scale used to weigh displaced water and the pressure of the initial product gas (which should be zero).

Following priming, the syringe pump is set in motion and feed is first diverted back to the feed bottle for 10 sec (first slop time) followed by feed injection into the reactor for a preset time after switching back the three-way valve ahead of the syringe pump. Upon completion of injection, feed is diverted back again to the feed bottle for another 10 sec (second slop time). At the end of feed injection, counts begin for both liquid strip time and catalyst strip time. The former is chosen as 7 (liquid strip multiplier) times the feed injection time while the latter equals liquid strip time less 10 sec with a maximum 360 sec. The product flows are sent to the gas collection vessel through liquid receivers where high-boiling products are condensed.

Catalyst regeneration starts with valve switches at the end of the catalyst stripping cycle. Air flow begins and the reactor temperature is raised to ~715 °C. The CO_2 concentration is continuously monitored by the IR gas analyzer until it is below 0.3%. The air is turned off and the N_2 flow to the reactor is re-established at the end of regeneration. The scale reading (mass of displaced water) is recorded along with pressure and temperature of the gas in collection vessel followed by gas mixing and warming (to ~30 °C). At this stage, the liquid receiver for the run can be removed manually from the system for subsequent handling if desired. The line between the collection vessel and the GC is purged with product gas, and the loop is filled for the subsequent GC analysis. Cool the reactor until the skin temperatures are 50 °C below their reaction set points and save all the data for the completed run. Return the unit to the first step of the test sequence for a new run, or discharge the spent catalyst to the waste vessel if it is the last run.

The established protocol proves successful in production of transportation fuels from canola oil in a blend. Good material balances (mass recoveries) are obtained in this study with a mean of 99.35% and a standard deviation of 0.31% from 18 LTU runs (**Table 2**). The conversions and yields from duplicate runs at 11.25 C/O ratio for each feed at a given temperature are quite reproducible (**Table 2**). Several typical FCC phenomena and cracking characteristics often reported in literature were also observed in this study: (1) Catalyst poisoning by feed basic nitrogen[22-24], particularly pronounced for HGO at low temperatures (490 °C in this work). The effect can be reduced at higher temperatures or C/O ratios; (2) Availability or exhaustion of crackable components in the feed and liquid product. Those in the feed are usually called "gasoline precursors", defined as the sum of saturates and monoaromatics[20,25-28]; (3) Accessibility of catalyst acid sites to molecules; for example, incomplete decomposition of bulky triglyceride molecules at 490 °C while their broken linear fatty acids can easily penetrate catalyst pores and be cracked[6]; (4) Oligomerization of olefins[29] from fatty acids to form aromatics and coke; (5) Preferential skeletal isomerization of olefins to form branched compounds[23,29].

The protocol is largely based on the LTU operating manual. The procedures in the manual must be strictly followed, except as noted. Critical steps within the protocol include preparation of equilibrium catalyst (must be on-size and coke-free); reactor preparation (using a feed line that yields a constant injector height, either 1.125 or 2.125 inch); CO_2 analyzer calibration; preparation of the syringe (feed rate calibration) and liquid product receiver (weighing the long liquid receiver in a draft-free environment; maintenance of coolant temperature in -12 to -15 °C range); system pressure test (to ensure a leak-free environment); choices of suitable catalyst strip time and liquid strip multiplier; analyses of gases (refinery gas analysis) and liquid product (simulated distillation by ASTM D2887[18]); assignments of molecular weight 86 (versus 89 from ASTM D7964-14[30]) for C_5+ unresolved lump, and carbon-to-coke factor 1.0695 (versus 1.083 from ASTM D7964, which assumes that one mole of hydrogen is associated with one mole of carbon in the coke).

One modification in the protocol that deviates from the LTU operating manual and ASTM D7964-14[30] is that in the final step of weighing the liquid receiver, the stopper is quickly removed from and put back in the receiver to equalize the pressure before weighing. This allows release of excess N_2, which is trapped at coolant temperature. However, it may also risk the chance of losing some gaseous product. Theoretically, this step may reduce the mass balance by 2.71 mass% for a run at a C/O ratio of 10 in our study, assuming that 149 ml N_2 in the liquid receiver is trapped and expanding from -15 to 25 °C at 93.5 kPa (701 mmHg) atmospheric pressure. The result agrees with experimental values (versus decreases in mass balance by 3.10 and 3.22 mass% for runs at C/O ratio of 10).

This protocol has also been extended to blends containing 50 and 100 v% canola oil in HGO. The high rapeseed oil concentration appears to be harmful to the system, requiring more frequent changes of the injector than normal, especially when pure canola oil is cracked. At low concentrations such as the one presented in this study, fouling did not occur.

In addition, the LTU cannot be applied to biomass pyrolysis oil containing emulsified water, which can evaporate at high temperatures for extended periods. In this case, an alternative test unit[31] with a free but attachable syringe to deliver the feed is an option[12]. Also, the LTU cannot determine H_2S yield quantitatively due to the water displacement method used to collect gaseous products of which H_2S is partially dissolved in water. The alternative test unit modified to accommodate a gasometer consisting of two gas chambers (with pistons inside) in series was found to be satisfactory for this application[22,23].

The protocol has also been employed for HGOs from paraffin-rich shale oils from oil shale and light tight oils (LTO) produced by hydraulic fracturing technology. For some of the runs using the said LTU, the simulated distillation results show significant amounts of dissolved gases in the liquid products due to the waxy nature of the feeds, resulting in overestimated gasoline yields and conversions. It is therefore recommended to crack the paraffinic feeds in the alternative test unit mentioned above, which includes a degassing step after condensation of liquid product in the receiver[31]. The said alternative test unit is widely used to characterize performance of FCC catalysts due to its relative simplicity, flexibility, versatility, and low cost. Over the years, the test method involved has been expanded to provide additional information such as product selectivities and qualities, and the operating variable and feedstock effects[32]. With adequate precaution on interpretation, test results can be used to assess commercial plant performance[33].

Note that the above operational deficiencies using the LTU pertain to our existing particular model. As technology evolves, new products may overcome the problems discussed above.

Disclosures

The authors declare that they have no competing financial interests.

Acknowledgements

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