Powder Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Thermal cracking of canola oil in a continuously operating pilot plant

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ARTICLE INFO

Article history:
Received 25 April 2016
Received in revised form 22 September 2016
Accepted 13 October 2016
Available online xxxx

Keywords:
Thermal cracking
Vegetable oil
Renewable energy
Refinery technology
LCO
Fluidized bed

ABSTRACT

Thermal cracking of canola oil was investigated in a continuously operating pilot plant. The influence of different cracking temperatures (450 °C to 580 °C) on the product was observed with a final objective of maximizing LCO (light cycle oil). LCO can be used as diesel blend if a required quality is achieved. The pilot plant was constructed as a reaction/regeneration system with an internal circulating fluidized bed design. All experiments were conducted with canola oil at a feed rate of 2.5 kg/h. Silica sand was used as bed material. A 6-lump model was used for product characterization. The composition of gas (C_1–C_4), gasoline (saturated hydrocarbons, olefins, aromatics) and LCO (aromatics) was analyzed. In addition, the oxygen content of the liquid products was determined at cracking temperatures of 450 °C and 580 °C. The experiments show that the product distribution is heavily dependent on the cracking temperature. With increasing cracking temperature gas, gasoline and carbon oxides increase, whereas LCO, residue and coke decrease. At a cracking temperature of 450 °C 8.6 wt% gas, 21.1 wt% gasoline, 47.5 wt% LCO, 15.8 wt% residue, 3.7 wt% coke and 3.3 wt% carbon oxides are formed. The liquid product contains high amounts of oxygenates.

1. Introduction

Europe's petroleum refining industry is challenged by increasing middle distillate demands, stagnating gasoline markets and stricter environmental regulations [1]. In addition, European politics enforce a systematic substitution of crude oil by renewable energy sources [2]. Existing refinery plants and processes are optimized in order to meet these requirements.

FCC (fluid catalytic cracking) is a well-established conversion process in petroleum refineries. It is used to convert heavy hydrocarbons into economically valuable products such as gaseous olefins, high-octane gasoline as well as LCO (light cycle oil). LCO can be used as diesel blend if a certain quality is achieved. Main quality issues are low amounts of aromatics and sulfur. These requirements are not fulfilled at common FCC operating conditions using a standard feedstock like vacuum gasoil. Hydro treatment of the vacuum gasoil or of the formed products is necessary to meet the environmental regulations. FCC is a flexible process. Yield and composition of the products can be influenced to a certain degree. Considerable influence possibilities include operation at suitable process conditions and proper selection of catalysts and feedstocks.

At Vienna University of Technology Reichhold and Hofbauer developed a reaction/regeneration system with internally circulating fluidized bed design. This continuously operating pilot plant was optimized for catalytic cracking. It allows high comparability with large-scale FCC plants [3]. Results can therefore be viewed with more confidence than e.g. micro activity tests. Detailed information of the pilot plant can be found in [4].

In recent research, the pilot plant was used for LCO maximization studies with different vegetable oils. The possibility to use these vegetable oils for catalytic cracking has been confirmed by various studies [5–9]. Vegetable oils were selected as an alternative to vacuum gasoil due to a number of advantages. They are CO_2-neutral and easy obtainable. The relatively high chemical similarity to diesel (compared to vacuum gasoil) qualifies vegetable oils as a high potential for satisfying LCO yields and qualities. The sulfur content is substantially lower (<25 ppm) [10]. Vegetable oils can also be processed at temperatures below 480 °C due to their different boiling situation. Mild process conditions (e.g. low cracking temperatures) increase the yield of the organic liquid product [7]. Catalytic cracking studies of soybean oil and palm oil at mild conditions provided promising results [11]. However, large amounts of aromatics were detected in the liquid product even though vegetable oils were used. It became apparent that the selection of the catalyst has a high impact on the product composition. Catalytically less or even non-active bed materials can be used to address this issue without fundamental changes of the process or the pilot plant. The general assumption is that thermal cracking of vegetable oils may yield more liquid products (especially LCO) with low aromatic content [12–14].

The objective of this study is to perform thermal cracking of canola oil in a continuously operating pilot plant. A focus is given to the optimization of LCO yield and quality. The FCC pilot plant was adapted to be able to use silica sand as bed material. Silica sand is not catalytically active and

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http://dx.doi.org/10.1016/j.powtec.2016.10.030
0032-5910/

Nomenclature

d_i	Particle diameter (class i) [μm]
$d_{p,mean}$	Mean particle diameter [μm]
FCC	Fluid catalytic cracking
FID	Flame ionization detector
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatograph
LCO	Light cycle oil
$\dot{m}$	Mass flow [kg/s]
TCD	Thermal conductivity detector
TFY	Total fuel yield
U_{mf}	Minimum fluidization velocity
VGO	Vacuum gasoil
x_i	Weight fraction of particles (class i) [1]

acts as both a heat- and a coke-carrier into and out of the cracking zone. Canola oil was chosen due to its high market share and its domestic importance. Experiments were conducted at a feed rate of 2.5 kg/h and at cracking temperatures between 450 °C and 580 °C. A 6-lump model is used for product characterization. The composition of gas, gasoline and LCO was analyzed in detail. The oxygen content of the liquid products at cracking temperatures of 450 °C and 580 °C was determined.

2. Experimental setup

2.1. Pilot plant

A schematic drawing of the pilot plant is shown in Fig. 1. The pilot plant was constructed as an internal circulating fluidized bed system. Thus, both reactors (riser, regenerator) are built in one apparatus, which results in a compact design.

The feed is preheated in a tubular oven, enters the plant through the feed inlet pipe and gets in contact with hot bed material. The feed evaporates instantaneously resulting in a fast upwards expansion. Thermal cracking reactions begin. Particles are sucked into the riser and are transported pneumatically to the top. Coke, which emerges during the cracking reactions, is deposited on the surface of the particles. At the riser outlet, these particles are separated from the product gas by a conical particle separator. Thermal cracking occurs in the riser reactor as well as in the insulated product gas section. The product gas exits the pilot plant on top and is burned in a flare. A minor part of the product is guided through a special condensation apparatus. The accumulated gaseous and liquid products are gathered and analyzed. In the pilot plant, after the separation, the coke-loaded particles move down a return flow tube. They are transported through the syphon into the regenerator zone. The regenerator is fluidized by air and is operated as a stationary bubbling fluidized bed. Coke is burned off in the regenerator. The particles are then guided through a cooler system and return to the bottom, where the cycle is repeated. This allows a continuous operation of the pilot plant.

Nitrogen is used as fluidization gas, except for the regenerator fluidization. Syphon and bottom fluidization both act as an improvement of steady particle circulation and as a gas barrier between regenerator and riser zone. Syphon fluidization also provides a certain strip effect of porous particles in the return flow tube.

Specific data of the pilot plant are given in Table 1. Feed rate, particle circulation rate, riser temperature and regenerator temperature can be adjusted in the given range. The mean residence time of the product gas in the pilot plant is about 20–80 s.

2.2. Feedstock & bed material

The main components of vegetable oils are triglycerides, which consist of a glycerol body with three fatty acid chains connected via carboxyl groups. Pretreated canola oil was used as feedstock. It was obtained from Rapso Österreich GmbH (Aschach, Austria). Canola oil plays an important role in domestic and global vegetable oil markets. It consists mainly of unsaturated triglycerides. Important properties and the fatty acid composition of canola oil are given in Table 2.

Silica sand was used as bed material. It was obtained from Quarzwerke Österreich GmbH (Melk, Austria). Physical properties and a chemical analysis of the used silica sand are given in Table 3. Silica sand can be classified as Geldart Group B. The particle size distribution is shown in Fig. 2. The mean particle diameter, calculated as follows, is about 112 μm.

$$d_{p,mean} = \frac{1}{\sum \frac{x_i}{d_i}}$$

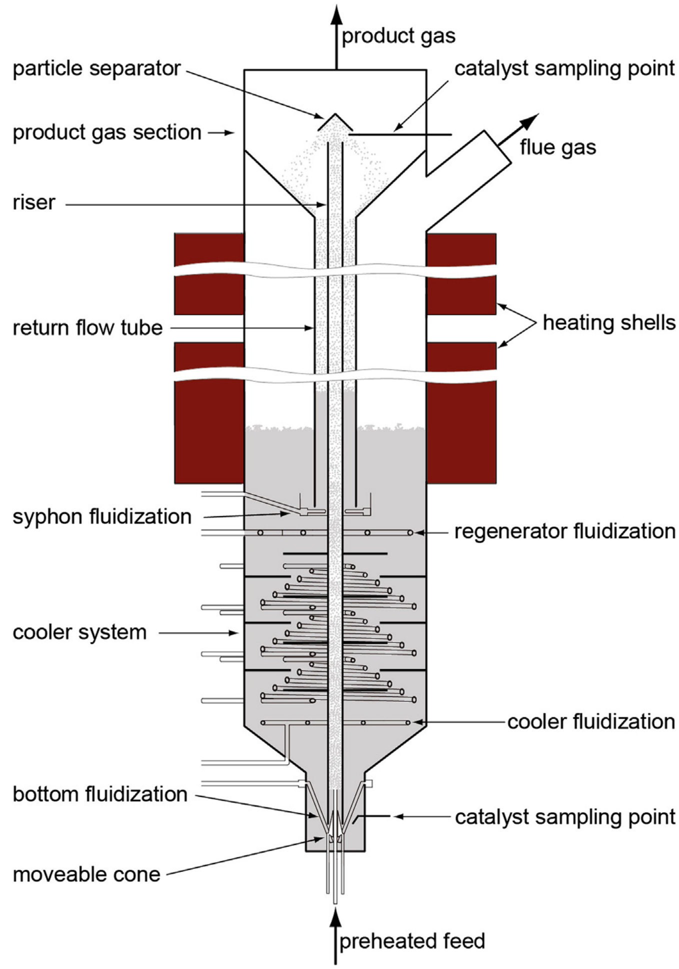

Fig. 1. Scheme of the pilot plant.

Table 1
Specific data of the pilot plant.

Feed rate	2–8 kg/h
Particle circulation rate	0.5–5 kg/min
Riser temperature	400–650 °C
Regenerator temperature	600–800 °C
Mean feed residence time	20–80 s
Reactor height	3.2 m
Reactor diameter	0.33 m
Riser height	2.5 m
Riser diameter	0.0215 m
Amount of particles	40–70 kg
Pressure	Atmospheric

Please cite this article as: J. Fimberger, et al., Thermal cracking of canola oil in a continuously operating pilot plant, Powder Technol. (2016), http://dx.doi.org/10.1016/j.powtec.2016.10.030