Fuel 106 (2013) 632–638

Contents lists available at SciVerse ScienceDirect

Fuel

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

Catalytic cracking of light gas oil using microwaves as energy source

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HIGHLIGHTS

- ▶ Catalytic cracking of light gas oil using microwaves (2.45 GHz) as the energy source.
- ▶ Catalytic cracking tests were performed in a spouted-bed reactor partially filled with zeolitic catalyst.
- ▶ The chromatogram obtained for the condensate oil (reaction product) is similar to that of a commercial diesel fuel.

ARTICLE INFO

Article history:
Received 29 May 2012
Received in revised form 30 November 2012
Accepted 4 December 2012
Available online 20 December 2012

Keywords:
Catalytic cracking
Diesel fuel
Light gas oil
Microwave
Spouted-bed

ABSTRACT

Catalytic cracking is a process of utmost importance in a refinery because it yields products of commercial interest from lower aggregate value oils. It is a high-return process and requires constant technological innovations to address environmental concerns. In this regard, an interesting alternative to conventional fluidized catalytic cracking processes, where the coke deposited on the particle surface is burned through combustion, is to heat the particles directly using microwave energy. Electromagnetic waves cause the dielectric heating of zeolite catalyst particles, providing the energy required for cracking reactions. Catalytic cracking experiments with microwaves were performed in a light gas oil obtained from vacuum distillation, in order to verify the effects of the feed temperature, catalyst mass, wave action time and nitrogen injection. The samples obtained were analyzed by gas chromatography and mass spectroscopy and sulfur determination was carried out by X-ray dispersion. It was demonstrated cracking reactions in the gas oil could be generated by using microwaves. An increase of 7.06 percentage points in the concentration of n-paraffins and isoparaffins could be obtained for volatile compounds at 200 °C, generating products with chemical characteristics similar to those of a commercial diesel. A significant decrease in the sulfur content also occurred, from 6751 to 2850 ppm. A spouted-bed reactor, inserted in a cavity designed to be multimodal, provided the best conditions of those evaluated for the reaction in a three-phase bed, operating with commercially used zeolite catalyst particles with an average size of around 68 μm.

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1. Introduction

To meet the demands for high-octane gasoline, jet fuel, and diesel fuel, components such as residual oils and fuel oils are converted to gasolines and other light fractions. Fluidized catalytic cracking (**FCC**) is a refining process which converts heavy distillates (gas oil and residues) into lighter fractions, such as diesel, gasoline and liquefied petroleum gas, by breaking large petroleum molecules into smaller ones. These reactions are endothermic and require a considerable input of energy. In conventional **FCC** processes, the energy required is transferred into the solid catalyst (zeolite) by burning the coke deposited on its surface during the process [1]. However, an alternative to heating the **FCC** catalyst through these combustion reactions is to heat the particles using microwave energy. Electromagnetic waves cause the dielectric heating of the zeolite surface, and they do not heat up the surrounding fluid; therefore, only the zeolite catalyst is heated, minimizing the thermal cracking of the fluid phase and, as a consequence, the formation of coking over the catalyst is lower [2].

Catalytic cracking reactions differ from thermal cracking reactions. The process of thermal cracking occurs at temperatures above 500 °C, favoring the formation of free radicals due to pyrolysis of the hydrocarbons. Most catalytic cracking reactions are ionic processes which occur at temperatures of around 450 °C, involving the formation of carbocations on the surface of a catalyst [3]. The chemical reactions that occur on the surface of the zeolite catalyst,

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http://dx.doi.org/10.1016/j.fuel.2012.12.024

Nomenclature

ρ	specific gravity
AD	apparent density
$\mathbf{A_M}$	microwave action
APS	average particle size
Cp	specific heat
C/O	catalyst/oil ratio
CS	cell size
FBP	final boiling point
FCC	fluidized catalytic cracking
$\mathbf{I_n}$	nitrogen injection
IBP	initial boiling point
LGO	light gas oil
LOI	loss on ignition
m_{res}	residual oil mass
m_{cat}	catalyst mass
m_{oil}	mass of light gas oil initially fed into the reactor
m_{con}	condensate oil mass
P	power density
PV	pore volume
REE	rare-earth element
T_e	feedstock temperature
T_f	final temperature
T_i	initial temperature
T_{out}	gas average temperature at the reactor outlet
T_{ave}	reactor surface temperature
t	time of microwave action on the water sample
t_r	operating time
TSA	total specific area

where there are "hot spots", are predominantly reactions with ionic mechanisms [3–6]. Lam et al. [7] used non-catalytic carbon particles to absorb microwave energy and promote the pyrolysis (thermal cracking) of waste oil.

The use of microwaves offers considerable advantages over traditional thermal heat sources in industrial processing, namely rapid heat transfer, volumetric and selective heating, compact equipment, rapid on-and-off action and pollution-free operation as no combustion is involved [8].

The application of microwaves in chemical reactions began with the studies of Gedye et al. [9], who compared using microwaves in organic synthesis with the classical procedures (hydrolysis, oxidation, esterification). Microwave energy has been applied in the petroleum industry and other areas such as mineral treatment processes [10–12], pyrolysis [13] and transesterification [14,15]. Studies by Al-Mayman and Al-Zahrani [2] demonstrated that when radio frequency (27.12 MHz) heating is utilized in catalytic cracking and the feed contains sulfur, this is converted almost in its entirety to sulfidric gas, concentrated in the gaseous phase, which is easily separated from the liquid fractions obtained. Furthermore, the hydrocarbons were only converted to small olefins (hydrocarbons in the range C_2–C_4) and linear paraffins in the kerosene (C_{10}–C_{16}) and diesel (C_{15}–C_{20}) ranges.

A review article and others related to the application of microwaves to oil sands and petroleum have been published recently [16–19]. Several studies have been performed on microwave-assisted desulfurization [20–22]. Leadbeater and Khan [20] investigated microwave-assisted desulfurization of heavy and sour crude oil using iron powder as a catalyst. They reported that hydrodesulfurization using microwaves could be carried out under milder conditions compared to the process of conventional heating.

Microwaves have a higher frequency and are more energetic than radio waves. They are generated by an oscillating electric field generator. This oscillation is selective to the ionic molecules [23] and can lead to different interactions between the zeolitic catalyst and the carbocations in the gas oil film present on the catalyst surface. Few studies using microwaves for catalytic cracking have been conducted, despite this being an alternative with great potential for application in the petroleum industry. Thus, the promotion of reactions in the catalytic cracking of light gas oil (**LGO**) was investigated using microwaves (2.45 GHz) as an energy source and the product obtained was compared with a commercial diesel fuel.

2. Experimental

2.1. Materials

Brazilian **LGO**, supplied by Petrobras-REPAR, was used as feedstock for the experiments and its characteristics are shown in Table 1. **LGO** is the lightest fraction obtained from vacuum distillation which is characterized by boiling in the range of 215–337 °C [24].

The formulation of an **FCC** catalyst is tailored to the specific needs of each refinery. Normally, an **FCC** catalyst consists of a zeolite (synthetic faujasite type Y), which is responsible for its activity and selectivity, and a matrix, responsible for the physical characteristics of the catalyst. Zeolites are crystalline microporous solids containing cavities and channels of molecular dimensions. The catalyst employed was a commercial zeolite, SIRIUS 2580 ZOOM, whose characteristics are listed in Table 2.

2.2. Equipment

The power input of the microwave equipment was 1500 W and the microwave frequency was 2450 MHz. A multimode microwave oven cavity of rectangular shape, with the dimensions (x; y; z) = (35.0 cm; 34.0 cm; 22.0 cm), was adapted so that a spouted-bed glass reactor could be placed inside it, as shown in Fig. 1. The reactor was designed to operate in the three-phase bed mode, according to studies by Al-Mayman and Al-Zahrani

Table 1
Properties of the light gas oil.

Sulfur content	6751	ppm
Density at 20 °C	0.88398	–
Viscosity at 40 °C	5.630	$mm^2\ s^{-1}$
Viscosity at 60 °C	3.480	$mm^2\ s^{-1}$
Distillation vol.%		
IBP	204.0	°C
10%	254.0	°C
20%	276.0	°C
30%	293.0	°C
50%	314.0	°C
70 %	335.0	°C
80 %	342.0	°C
90 %	372.0	°C
FBP	435.0	°C

IBP – initial boiling point; **FBP** – final boiling point.

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