Ultrasonics - Sonochemistry 48 (2018) 103–109

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

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

A novel ultrasonic-assisted method for enhanced yield of light oil in the thermal cracking of residual oil

Guanlong Song[a], De-Hui Wang[b,*], Zhiwei Zhang[b], Mei Liu[b], Qian Xu[c,*], De-Zhi Zhao[b,*]

[a] School of Metallurgy, Northeastern University, Shenyang 110819, China
[b] College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shihua University, Fushun 113001, China
[c] School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Keywords:
Ultrasonic
Thermal cracking
Residual oil
Yield
Light oils

ABSTRACT

In this work, a novel ultrasonic-assisted thermal cracking method for improving the yield of light oil from the thermal cracking of Huizhou atmospheric residue (HAR) is proposed and demonstrated. To achieve this, a self-developed autoclave ultrasonic reactor (20 kHz; 200 W) was designed. Gas chromatography (GC), and elemental analyser (EA) were employed to analyse the composition of gaseous and liquid products after the cracking of residual oil. Compared to the traditional thermal cracking process under similar conditions (430 °C; 8 MPa; 2 h), the ultrasonic-based process produced lower gas products (*ca.* 0.6%), higher gasoline and diesel fractions (*ca.* 10%), vacuum residue, and lower yield of coke yield (*ca.* 4%). In addition, coke produced by the ultrasonic-assisted thermal cracking method exhibited spherical morphology with narrow size distribution and smooth surface with small amounts of adsorbents attached to it. The derivative characteristic peak (101 crystal face) at 2θ of 43.56° belonged to α-graphite. The abnormal high local temperature and pressure conditions produced by ultrasonication were the key factors for the thermal cracking of residual oil. The experimental results indicated that the ultrasonic-assisted thermal cracking can dramatically lead to higher yield of light oil, higher degree of cleavage, and more favourable reactions under the same conditions (as those of traditional thermal cracking). Therefore, compared to the traditional delayed coking process, the proposed ultrasonic-assisted technology can significantly decrease the power consumption. This study has vital significance in predicting and enhancing the performance of thermal cracking on a large scale.

1. Introduction

With the over-exploitation of crude oil, its reserves are depleting, due to which, the processing of residual oil is becoming more and more important in recent years [1,2]. Meanwhile, with the increasing demand for regulations to protect the global environment, the field of residual oil processing has become very challenging. The amount of processed residual oil using delayed coking process accounts for more than a third of the total processing volume around the world [3]. The delayed coking process consists of a typical thermal cracking method, and is one of the most effective methods to solve the problem of efficient residual oil's thermal cracking. However, the method has certain drawback, including extremely high-heart energy consumption, low yield of useful liquids, and reactors' or pipelines' clogging due to large amount of coking [4]. Therefore, an efficient method is sought to solve these problems for the process of traditional thermal cracking. However, only a handful of strategies for reducing coke, increasing the light oils, and reducing the energy consumption have been well established [5].

It is well known that ultrasonic irradiation can significantly improve the reaction efficiency of chemical reactions, which is mainly due to the acoustic cavitation when mechanical vibrations are produced and transmitted into the reaction medium as ultrasonic waves [6]. This phenomenon involves the formation, growth and implosive collapse of bubbles in the reaction medium, which is irradiated with high-intensity ultrasound, that creates shock waves, provides a unique set of conditions to promote the chemical reaction, and thus, increases the chemical reactivity in these systems. When the compression of bubbles occurs during cavitation, the short-lived localized hot spots can be generated. Bubbles collapse rapidly and violently during cavitation, thus providing temperatures of about 5000 K and pressures of about 1000 atm, with the heating and cooling rates of above 10^{10}·Ks^{-1} [7]. Although the phenomenon of cavitation lasts only for a few seconds and the amount of energy released by each bubble is minimal, the cumulative amount of energy generated is extremely high. This micro-environment, with extreme local conditions, is favorable to create

* Corresponding authors.
E-mail addresses: dhuiwang@aliyun.com (D.-H. Wang), qianxu@shu.edu.cn (Q. Xu), fszhaodezhi@163.com (D.-Z. Zhao).

https://doi.org/10.1016/j.ultsonch.2018.05.029
Received 9 February 2018; Received in revised form 6 May 2018; Accepted 22 May 2018
Available online 23 May 2018
1350-4177/

active intermediates such as alkyl and hydrogen radicals that allow the reaction to proceed instantaneously [8]. A great many researchers considered that the formation and collapse of ultrasonic microbubbles exert remarkable influence on the chemical and physical properties of most substances. Due to the development of cheap and reliable ultrasonic wave generators, the application of ultrasonic wave technology is growing in the fields of chemistry and chemical engineering, especially in oil extraction, oil-water de-emulsification, modification of asphaltene, desulfurization, reduction in the viscosity of heavy oil and applications in crude oil [9–19]. In particular, some studies have shown that ultrasonic or ultrasonic-assisted technology can control some cracking reactions, and that too accompanied by low energy consumption for the overall process. In a previous study, an ultrasonic reactor was used to modify a heavy hydrocarbon mixture. According to the distillation data of vacuum residuum, light components that boiling point below 350 °C increased by 55% [20]. Dalai and co-workers obtained lighter hydrocarbon gas, mainly consisting of methane, ethylene, ethylene and propylene, by processing heavy gas oil through ultrasonic technology under atmospheric pressure without using any additive [21]. Yen and co-workers studied the reaction pathway of asphalt under ultrasonic conditions, and showed that the pathway consisted of the conversion of cyclanes to paraffin hydrocarbon (cracking) or aromatic hydrocarbon (dehydrogenation) [22]. Cataldo reported that the cracking and pyrolysis of aromatic hydrocarbon and cyclanes occurred under ultrasonic conditions [23].

As delineated above, the successful applications of ultrasonic technology for thermal cracking encouraged us to further extend this excellent research. Most of the previous works focused little on the detail about the influence of ultrasonic waves on the physical properties as well as the morphology of coke produced from the cracking of asphaltene. As a continuation of our research on the oxidative desulfurization using ultrasound technology [24], we herein first report a new designed autoclave ultrasonic experimental apparatus, which contain an ultrasonic generator. The ultrasonic generator is selected in the reactor by a probe-type which can bear high temperature and pressure (500 °C and 20 MPa). These necessary units were introduced as trigger sites to realize efficient ultrasonic-assisted process for enhancing the yield of light oil in the thermal cracking of inferior residual oil. In addition, the experiments of the family composition of gas, liquid and solid products were also analyzed. Compared to the traditional delayed coking process, new ultrasonic-assisted technology can significantly decrease the overall power consumption for the cracking process. To the best of our knowledge, the self-developed reactor (reported herein) is the first ultrasonic-assisted autoclave reactor reported in literature and used for the thermal cracking of residual oil.

2. Experimental

2.1. Properties of raw oil

The raw oil used in this work was obtained from Huizhou refining company (China Offshore Oil Corporation), and was atmospheric residual oil (HAR). The composition and properties of raw oil are presented in Table 1. It can be seen that the HAR is difficult to be processed further, and this was due to its higher viscosity, residual carbon, and metallic content.

2.2. Materials and instruments

The experimental apparatus included the reaction system and the feedstock system, as shown in Fig. 1. The reaction system contained of two parallel reactors, one of which was a traditional reactor (Reactor a), which was used for the traditional thermal cracking, while the other (Reactor b) was designed for ultrasonic-assisted cracking process. The Reactor a included a high-pressure stirring autoclave having the volume of 500 mL, and the temperature and pressure settings of 550 °C and 25 MPa, respectively (Fig. S1). The Reactor b had the volume of 500 mL, with the temperature and pressure settings of 500 °C and 20 MPa, respectively (Fig. S2). The ultrasonic generator was applied during the reaction using a probe-type device with the frequency of 20 kHz and input power of 200 W. All the reactions took place at atmospheric pressure.

The yields and compositions of gaseous products were determined using a gas chromatograph (7890A, Agilent Technologies, America). The elements composition of HAR was determined using a C/H/N/S elemental analyzer (2400II, PerkinElmer, America). The coking morphologies were recorded using an optical microscope (BX-51, OLYMPUS, Japan) and scanning electron microscopy (SEM) (JSM-7500F, Hitachi, Japan). The X-ray powder diffraction (XRD) spectra were recorded using a Rigaku D/Max-2500 X-ray diffractometer (Cu K radiation = 0.15405 nm), with silicon (99.999%) as the standard for peak broadening. The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using an Agilent Cary 660 infrared spectrophotometer.

2.3. Methodology

Raw oil samples (240 g) were placed in two reactors, which were purged thrice using N_2. After purging, H_2 was pumped into the reactors for maintaining the pressure of 8 MPa. Then, the two parallel reactors were heated to 100 °C. The stirrer and ultrasonic wave generator were switched on. The temperature was increased to 380 °C and maintained at this value for 20 min. After that, the two reactors were successively heated to 400, 410, 420, 430 and 440 °C, respectively. When the reactions finished after 2 h, the samples were cooled to 30 °C. The gas components of the reaction products, the liquid in the buffer tank and the reactors, the solid products in the reactors, and the stirring bar (or ultrasonic wave transmission bar) were collected for further characterization. All the experiments and measurements were performed at least in triplicate and average values were used for further analysis and calculations.

3. Results and discussion

3.1. Comparison of gaseous compositions

Fig. 2 shows the yields of gaseous products from the cracking of residual oil using traditional and ultrasonic-assisted thermal cracking processes at different temperatures. In the traditional thermal cracking process, the yield of gaseous products increased from 0.89% to 6.55% when the reaction temperature from 400 °C to 440 °C. Meanwhile, for the same increase in temperature (from 400 °C to 440 °C), the yield of gaseous products increased from 0.83% to 5.92% using the ultrasonic-

Table 1
Properties of HAR.

Parameter	*Mn*	*w*(CCR)/%	*w*/%			*w*(Metal)/(μg·g^{-1})		*w*(SARA)/%			
			C	H	S	Ni	V	Saturates	Aromatics	Resins	Asphaltene
Feed	818	15.51	86.22	11.29	0.48	113.2	2.0	47.35	29.57	22.93	0.15

CCR = Conradson Carbon Residue.