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The effects of microwave plasma torch on the cracking of Pyrolysis Fuel Oil feedstock

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HIGHLIGHTS

- Pyrolysis Fuel Oil (PFO) was processed by Microwave plasma torch.
- The power and flow rate of carrier gases on the cracking operation were studied.
- The increase of the power results in more products.
- The production rate of products increase with increasing the flow rate.

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ABSTRACT

Cracking of Pyrolysis Fuel Oil (PFO) using a microwave plasma torch in liquid has developed a new process for production of valuable petrochemical hydrocarbons. Main parameters, including the power and flow rate of the carrier gases on the cracking operation were studied. The major products obtained were hydrogen and light C_1, C_2, C_3, and C_4 hydrocarbon compounds. Increasing of the power and gas flow improved the cracking of PFO, but, they were unable to change the selectivity of products. Optimal conditions were 850 W for power and 5000 sccm (ml/min) for flow rate and the production rate of C_4 and H_2 were 27.37 sccm and 446.31 sccm, respectively.

1. Introduction

The fuel oil portion of ethylene cracker effluent is an incredibly complex, probably millions of compounds, wide-boiling mixture. It is full of olefins, diolefins, triolefins, aromatics, polynuclear aromatics, etc. throughout the boiling range. Cracked fuel oil (CFO) or Pyrolysis Fuel Oil (PFO) in the range of C_6–$C_{>40}$ long hydrocarbon chains, particularly aromatic, resin and asphaltene, semi-solid material and some sulfur and metal contaminants are general classification for the petroleum heavier oils in refinery operations. The complexity of the structural chemistry of heavy oil is responsible for most of the challenges associated with these feeds. It is estimated that a single heavy oil feed contains hundreds of thousands of components consist of C_6-200C.

Since the supplies of natural hydrocarbons are limited, the conversion (reforming, cracking, upgrading) of inexpensive fuel oil to valuable petroleum products with greater economic value is very important for a variety of applications.

In cracking process, it is necessary to get various useful hydrocarbon gases and oils. Since petroleum is very complex in its intermolecular forces among individual species, such as association, assemblage, aggregation, and interaction, it is impossible to identify each individual component and its upgrading chemistry. The current state of the art for upgrading heavy oil can be divided into two general approaches: hydrogen addition and carbon rejection, which relate the thermal or catalytic cracking of petroleum feedstocks to their fractional composition.

In many practical engineering applications, the novel technology of plasma and catalytic processes were studied by many researchers as a promising conversion method for different kinds of hydrocarbons [1–4], including some studies on reforming of methane in AC microsized gliding arc discharge [5], ethanol steam reforming [6], non-oxidative conversion of methane into higher

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hydrocarbons with two concentric dielectric barriers [7], oxidative reforming of simulated biogas to produce high-concentration syngas by using novel plasma shade [8] and reforming of heavy oils [9–12]. Plasma technologies compete with other approaches and successfully find their way in modern industry. Plasma cracking process can be configured to operate at ambient temperature and atmospheric pressure unlike the traditional non-catalytic cracking processes. Moreover, plasma methods have a possibility of fuel cracking control, producing various carbon compounds. The plasma process also benefits refinery operations by reducing operation and maintenance costs, as well as environmental liability costs, and high production yields.

In more recent papers published by Rahimpour and co-workers [13–16], a nanosecond pulsed dielectric barrier discharge plasma reactor has been investigated for conversion of heavy naphtha to light gaseous hydrocarbons in the range of C_1–C_3 and H_2. They reported that the highest process efficiency has been obtained at 7 kV and 18 kHz which was 79.38 l kW h^{-1} (l/kW h) for 1 ml/min^{-1} of feed injection and 24.70 W input power. Their results indicate that the hydrocarbon product distribution during the process is ethylene $\gg C_2 > C_1 \gg C_3$. In a further study by these authors, they reported that non-thermal plasma (NTP) is effective in cracking of C_1–C_{16} straight-chain alkanes from light gaseous to heavy hydrocarbons into hydrogen.

The new method of plasma processing which is under investigation involves the generation of plasma within oil by means of mobile charge carriers controlled by an external electric field. The use of quasi-equilibrium low temperature (arc, radiofrequency, and microwave) plasma intensifies the high temperature processes of pyrolysis and conversion of hydrocarbons. These processes add carbon and hydrogen simultaneously to heavy oil during upgrade in a single step. Heavy oils and hydrocarbon gases go into a reactor, and lighter synthetic crude oils and transportation fuels come out.

Numerous attempts to use atmospheric-pressure pulsed discharge non-equilibrium plasma have been reported. In 2006, Nomura et al. [17] used six types of liquids in the microwave plasma: n-dodecane, benzene, waste cooking oil and waste engine oil under normal conditions to obtain the higher deposition rate. In experiments carried out by Garifzyanova [18] the synthesis of C_2 in plasma-chemical pyrolysis of heavy residue of high-viscosity, high-sulfur crude (HSC) as an additional source of feedstock for the petrochemical industry by using four different catalysts such as industrial carbon (IC), K-24I, and alumina Al_2O_3 has been investigated. His results showed that the degree of conversion of feedstock increased to 83, 4% when 1–5 wt.% catalyst was added to it. C_1–C_3 (acetylene, ethylene, methane propylene, propane, etc.,) were the basis components of the pyrolysis gas.

In another work, by Zhivotov et al. [19] the effect of atmospheric-pressure microwave plasma torch on the process of partial oxidation kerosene ($C_{11}H_{22}$) with air oxygen was examined. They reported that a continuous microwave discharge has a better effect on the process of kerosene conversion into synthesis via the partial oxidation reaction than the equivalent thermal energy input via the combustion of a portion of the fuel. The effect of the discharge reduces to the heating of the reactants at the flame front, i.e., in the region with the maximum temperature of the process.

In response to the above mentioned challenges, the chemistry of fuel oil upgrading is extremely complicated and it is necessary to research new ways for heavy oil cracking by plasma technology for in situ light valuable petrochemical products. Therefore, in this study, the application of quasi-equilibrium microwave plasma for cracking PFO is investigated. We propose to apply plasma in liquid instead of gas phase plasma. A rector for producing microwave plasma in a liquid could produce plasma in hydrocarbon liquid and waste oils. A microwave plasma system was designed and constructed. Using this technology as a chemical reactor we expect to produce large amounts of petrochemical valuable gases. We confirmed that fuel gases such as C_2, C_3, C_4, and H_2 can be produced by microwave plasma in liquids.

Most researches have been conducted on the pure liquid, but we worked on a complex mixture of petroleum liquids. In more researches DBD (dielectric barrier discharge) has been used for working on liquids, while microwave is newer than DBD for working on liquids. Working on fluids by using microwave is a new technique considered in this study but the data of microwave on liquid is limited. Our approach in the present work is to present a new type of non-catalytic – non-thermal microwave plasma torch (MW Torch) to convert PFO to valuable petrochemical products, for the first time, using argon as the working gas. The main purpose of this study is to find the optimum conditions by varying the effects of input power and gas flow rates on the quantity and quality of cracking products. The production efficiency is improved by increasing the power and flow rate. This detailed study offers new insights into the cracking process of these parts of heavy fuel oils.

2. Experimental

2.1. Experimental analysis of Pyrolysis Fuel Oil

The compositions of PFO fraction are very complexes of paraffin, naphthenes and aromatics. Table 1 gives the percent by mass (wt.%), of the most common components in a representative sample of the fuel oil. These fuel oil hydrocarbons were analyzed by gas chromatography (GC–DHA; Varian CP-3800, capillary column SilPona CB) equipped with flame ionization detector (FID); GC/mass spectroscopy (GC–MS; Varian CP-3800, Column CP-Sil 8) for quantitative and qualitative analyses.

Fig. 1 shows the distillation curve of the sample fuel oil at different temperatures. The distillation range of heavy oil is between 100 °C and 650 °C. In Fig. 1, the percentage yield of the distillation product slightly increases between 230 °C and 600 °C. This product consists of aromatics hydrocarbons with about 10 up to 30 carbon atoms in compounds. The average chemical formula for fuel is C_{15}'s, ranging from approximately C_{10} to ~C_{18}'s. Fig. 2 shows the Chromatogram of fuel oil.

Since fuel petroleum contains literally thousands of hydrocarbon compounds, separation of the fuel into pure compounds is neither feasible nor necessary. Fuel cracking using plasma is one of the methods to enhance combustion by forming lighter hydrocarbons and hydrogen from heavier ones.

2.2. Microwave torch reactor setup

The schematic view of the microwave plasma torch system is shown in Fig. 3. Basic configuration for the abatement system consists of a power supply (2.45 GHz, 2 kW), a microwave generator (magnetron), rectangular waveguide components, including an isolator, a three-stub tuner, a plasma applicator, a short-circuit plunger, and a gas-supplying system. The microwave generated by magnetron travels through the rectangular waveguide. The

Table 1
Percent by mass (wt.%) of most common composition of fuel oil.

Components	wt.%	Carbon number
Aromatics	40.586	C_6–C_{18}^+
Iso-paraffins	10.896	C_6–C_{11}
Naphthenes	1.496	C_7–C_{13}
Olefins	9.977	C_6, C_8
Paraffins	1.773	C_{10}–C_{16}
Unknown residue	35.272	C_{14}–$C_{>40}$
Total	100	