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# Characterization of pitch derived from pyrolyzed fuel oil using TLC-FID and MALDI-TOF

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## HIGHLIGHTS

- TLC-FID and MALDI-TOF analysis for petroleum-based pitch.
- Characterization of molecular weight segment changes during PFO thermal reaction.
- Correlation of thermal and chemical properties based on asphaltene formation for pitch synthesis.

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## ABSTRACT

In this work, pitch was synthesized by a thermal reaction of pyrolyzed fuel oil (PFO), and its thermal properties were characterized using thermogravimetric and softening-point analyses. Thin-layer chromatography-flame ionization detection (TLC-FID) was performed to identify the saturated, aromatic, resin, and asphaltene (SARA) fractions to better understand the characteristics of the pitch produced during the high-temperature reaction of PFO. In addition, MALDI-TOF analysis was adapted to confirm the molecular weight segment. During the reaction, the thermal properties of the prepared pitch were determined as a function of the reaction time and temperature. The asphaltene fraction was generated as the aromatic fraction of the material decreased. The pitch properties were observed to be a function of the changes in the molecular weight distribution due to processes such as distillation, condensation, and cracking.



## 1. Introduction

Refinery capacities have continued to increase with the development of the petroleum industry. An inevitable consequence is that the amount of petroleum residue is also increasing as a by-product of the refining process. The quantity of petroleum residue is estimated at more than 810 million metric ton per annum (MMTPA) worldwide [1]. It is well known that petroleum residue consists of many complicated polycyclic hydrocarbon compounds, including more than thousands species with many impurities, such as S, N, Ni, V, and ash [2,3]. The chemical composition of this residue makes it very difficult to convert it into a more valuable product.

Regardless, petroleum residue is an attractive material with great potential due to an abundance of polycyclic hydrocarbon compounds that may be converted into more valuable petroleum products. Thus, various studies have been conducted to improve the applicability of petroleum residue. Two representative reactions that can process petroleum residue are visbreaking and the delayed coking processes [4–6]. Visbreaking is one of cracking methods including the thermal reaction to decompose the heavy polycyclic hydrocarbon compounds under severe conditions at high temperature (generally, >300 °C). Delayed coking is a process used to manufacture needle coke, which is one of the main materials to produce synthetic graphite. The common denominator of these two processes is that each operation is being conducted at high temperature above 300 °C. A highly condensed polycyclic hydrocarbon compounds known as pitch can be formed by these above reactions.

Pitch is an intermediate material between petroleum residue (a liquid) and coke (a solid), and it is a liquid–crystalline material that does not possess crystallinity. It is prepared in a high-temperature reaction of approximately 300–400 °C before coke is formed. The

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mechanism of pitch formation is also known as the polymerization, aromatization, and condensation of aromatic compounds [7,8]. The properties of the formed pitch can indicate whether the visbreaking and delayed coking reactions mechanism occur, which depends on the operational conditions. The quality of pitch and coke is determined based on operation conditions. Accordingly, it is necessary to develop analytical method for further understanding the characteristic of pitch. However, most conventional analytical techniques (Gas chromatography and Liquid chromatography) are limited by the volatility and solubility of the samples for adapting the analysis of high condensed aromatic materials [9]. Therefore, further adapted analytical method is needed to understand the chemical characteristic for pitch derived petroleum residue having high molecular weight components.

Thin-layer chromatography-flame ionization detection (TLC-FID) is especially useful in separating the maltene (saturated, aromatic, and resin) and asphaltene phases in heavy oil according to the solubility and differences in affinity in a solvent [10]. Asphaltenes are the insoluble fraction of the heavy oil that consist of heavy molecular species [11]. The molecular structure and weight of the asphaltenes have been suggested in various studies [12–14]. It has been determined that asphaltenes (in heavy oil) have similar condensed chemical structures and molecular weights as pitch, despite the dissimilar feed origin and experimental conditions. In this study, TLC-FID was used to characterize pitch and identify the SARA-fraction changes during high-temperature reactions occurring above 350 °C.

Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) is an analytical method based on soft ionization. The Mark group at Clemson University recently adapted MALDI-TOF for petroleum analysis and optimized the sample-preparation method and analysis conditions [15–17]. MALDI-TOF has the ability to analyze polycyclic hydrocarbon compounds, especially those with high molecular weights.

This study provides empirical information about the pitch-formation phenomenon and chemical characteristic of pitch as a result of a thermal reaction of PFO, based on SARA classification and the molecular weight distribution. The pitch derived from the petroleum residue was synthesized by controlling the thermal reaction conditions without coke formation. The chemical and structural changes of the pitch are discussed based on TLC-FID and MALDI-TOF analyses to better understand the phenomenon of pitch synthesis during high-temperature reaction.

## 2. Experimental setup

### 2.1. Materials

PFO, which is a by-product from naphtha cracking process, is yielded over 100 MMTPA in South Korea refinery industry and used as a low-cost plant fuel due to the difficulty of re-treatment process and low utilization. Nevertheless, the abundant aromatic contents and low impurities of PFO are attractive to utilize as a feedstock of pitch. In this study, PFO (Yeochun NCC CO. Ltd., produced by NCC (Naphtha Cracking Center), South Korea) was used as a pitch feedstock without any further purification. N-Hexane, toluene, dichloromethane (DCM) and methanol were used as solvents for TLC-FID. The compound 7,7,8,8-tetracyanoquinodime thane (TCNQ) was used as the matrix for MALDI-TOF.

### 2.2. Thermal reaction

A 5-L autoclave reactor was used to thermally react the PFO. Twin thermocouples with a proportional–integral–derivative (PID) controller system ensured that fluctuations were absent from the reaction temperature profile. The reaction temperature error was monitored and contained a programmed correction to within ±2 °C. Detailed reactor-system information is displayed in Fig. 1. The reaction procedure is as follows. First, 1500 g of PFO was stirred for 30 min with $N_2$ purging to remove any oxygen prior to heating the PFO. The reactor was heated and maintained according to the programmed temperature conditions. The reaction temperature and time were set as variable factors. Table 1 presents the detailed conditions and a list of the samples produced. The reaction temperature was set below 370 °C to avoid coke formation. All samples were examined to ensure 100% solubility in DCM. Finally, nine different types of pitch were obtained with zero coke content.

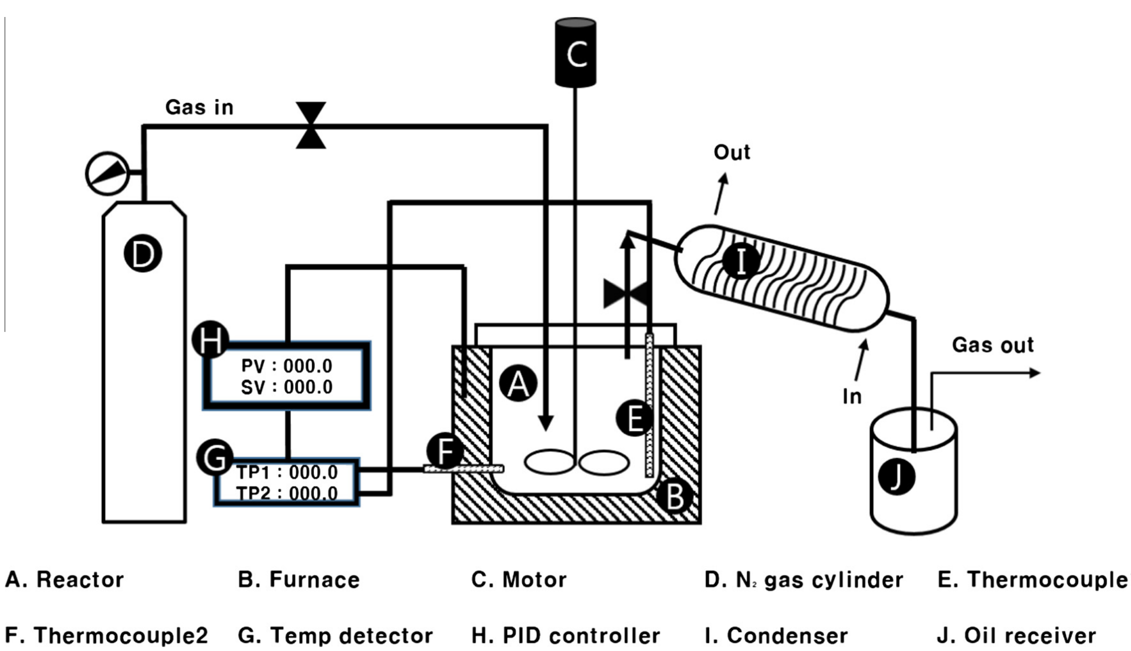


**Fig. 1.** Scheme for the 5-L-scale autoclave reactor system.