



Mild hydrotreatment of low temperature coal tar distillate: Product composition



Wei Tang, Mengxiang Fang*, Hongyan Wang, Panlong Yu, Qinhui Wang, Zhongyang Luo

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

HIGHLIGHTS

- Product composition is seriously influenced by thermodynamics equilibrium shift.
- Cycloalkanes and phenyl cycloalkanes are the primary hydrogenated product.
- Biaromatics are rarely transformed into monoaromatics unless at low LHSV.
- The incomplete hydrogenation is related to the methyl substituted on aromatic ring.
- A reaction scheme of aromatics is proposed based on the composition of product.

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ABSTRACT

The hydrogenation of low temperature coal tar was carried out over a MoNiWP/Al₂O₃ catalyst under mild conditions to produce clean liquid fuel. The effects of temperature, pressure and liquid hourly space velocity (LHSV) on product composition were determined by FT-IR and GC-MS analysis. The feedstock and products were classified into several groups according to saturation level to probe the reaction mechanisms of the main aromatic compounds in coal tar. At 375 °C, 6 MPa and LHSV of 0.4 h⁻¹, alkyl-phenols and alkyl-naphthalenes were transformed into cycloalkanes and phenyl cycloalkanes with the yield of 60.4% and 83.9%, respectively. The properties of feedstock were clearly upgraded after hydrotreatment. Methyl substitution on aromatic rings negatively influenced to the conversion of phenyl cycloalkanes to bicyclic alkanes by inhibiting hydrogenation of the aromatic ring. In contrast to previous research on model components, phenyl olefins appeared to be the final product of alkyl-naphthalenes hydrogenation. The transformation of bicyclic compounds to monocyclic compounds was insignificant. Based on these results, a reaction scheme of aromatic compounds in coal tar distillate was proposed.

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1. Introduction

As crude oil is being exhausted and the consumption of fuel oil rises, the demand of raw oil increases rapidly. More and more attention is paid on new resources, such as bio-oil, coal-derived liquid and oil shale. The resources of biomass are discrete and not suitable for industrial utilization. High water content and low heat value of bio-oil also restrict its spreading. As comparison, coal will be the chief energy source in China over the next few decades, and over 10 million tons of coal tar is produced within the country each year as a byproduct of coal pyrolysis [1]. Chemicals can be extracted from high temperature coal tar, and low temperature coal tar, which contains lighter fraction, is considered appropriate for producing fuel oil by hydroprocessing.

The coal tar hydrotreatment includes hydrogenation, hydrocracking and isomerization. Due to the high viscosity and complex

composition of coal tar, rigorous conditions of over 10 MPa and 400 °C are typically used for its hydrotreatment [2–4]. High hydrogen flow rate and low weight hourly space velocity have also been suggested [5]. Recently, it was proven that coal tar distillate could be hydrogenated to produce gasoline and diesel oil using serial fixed bed reactors under much milder conditions [6,7]. After removing pitch, which is difficult to convert into smaller molecules, coal tar distillate is easily transformed into clean liquid fuel.

Since coal tar is composed of hundreds of substances [8], it is difficult to trace the behavior of every compound. Many compounds in coal tar, including monocyclic aromatics [9,10], polycyclic aromatics [11–13], and heterocyclic compounds [14–16], have been extensively investigated on an individual basis. Girgis and Gates [17] reviewed the reaction networks and kinetics of hydrodearomatization (HDA), hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO). However, studies of individual model compounds cannot account for interactions between compounds likely to occur in coal tar. To learn more about such interactions, coal tar simulants using several

* Corresponding author. Tel.: +86 57187952803; fax: +86 57187951616.

E-mail address: mxfang@zju.edu.cn (M. Fang).

compounds with different functional groups have been studied. First order reaction rates and activation energies for the hydrogenation of polycyclic aromatics in anthracene oil have been calculated by Rosal et al. [18]. Wandas et al. [19] compared the hydrogenation products of cresol with and without naphthalene, finding that, isocompounds and novel reaction mechanisms were displayed in the presence of naphthalene. These differences could be attributed to tetralin, an intermediate of naphthalene hydrogenation. Nagy et al. [20] demonstrated that deep sulfur removal is necessary before hydrodearomatization process in order to obtain higher hydrodearomatization efficiency. Liu et al. [21] found thiophene is more effective than 4,6-dimethyldibenzothiophene for catalyst deactivation.

Though abundant research on model compounds has been carried out, the transformation between fractions is still not perfectly understood. During the transformation of coal tar to fuel oil, aromatics are typically hydrogenated to form saturated hydrocarbons, and heteroatoms like N, S and O were removed. The fuel oil yield can be remarkably influenced by reaction conditions. Qader and Hill [22] investigation on the effect of temperature on gasoline and diesel oil fraction in the transformation product showed that, gasoline yield increased and diesel oil yield decreased as temperature rose. Increasing pressure has also been found to produce a larger organic phase [23]. Supercritical solvents like gasoline introduced to improved the yield of light oil in a study by Gu et al. [24], produced optimal performance at 380 °C and 2 MPa. Thus, previous studies have mainly concentrated on the methods to obtain greater gasoline and diesel oil fractions. The effect of the same parameters on transformation of aromatics in coal tar during hydrotreatment at mild conditions has not been received as much attention.

To help build additional knowledge in this area, this study focused on transformation mechanisms between groups classified by saturation level and the generation of light fraction by hydrotreatment from a low temperature coal tar. In particular, we investigated the effects of temperature, pressure and space velocity on product composition. Based on the results, we also propose here a reaction scheme describing how the primary aromatics in coal tar distillate are affected by hydrogenation, isomerization and hydrocracking.

2. Experimental

2.1. The feedstock

A distillate of low temperature coal tar having a boiling point <300 °C was employed as the feedstock. A commercial low temperature coal tar was first produced through bituminous coal pyrolysis at 550 °C in a power plant. The feedstock was then obtained by distillation of this low temperature coal tar at atmospheric pressure using a 36/100 spinning band distillation system (Osbert International Inc.).

Coal tar distillate with a boiling point >360 °C is known as coal tar pitch, which is extremely difficult to be hydrogenated and can damage hydrogenation equipment. Distillate with boiling point from 300 °C to 360 °C is the anthracene oil fraction, which is composed of polycyclic aromatics. The intent of this study was to investigate the conversion of bicyclic aromatics to cycloalkanes and light ring-open products which strongly influence the yield and quality of gasoline and diesel oil. The transformation from polycyclic aromatics to bicyclic aromatics is easy to achieve [25]. We therefore chose to use a distillate with a boiling point <300 °C to avoid the influence of the polycyclic aromatics in anthracene oil fraction and simplify the analysis.

2.2. Characterization of the feedstock and hydrotreatment product

Elemental analysis of the feedstock and the hydrotreatment product was carried out on an Elementar Vario Micro (Germany). The chemical composition of the feedstock and the product was measured by gas chromatography-mass spectroscopy (GC-MS, Trace DSQ II) using an HP-5 capillary column (30 m × 0.25 mm × 0.25 μm, Agilent). Helium (99.999%) was used as the carrier gas at a flow rate of 1 mL/min with a split ratio of 1:20. The oven temperature was initially held at 40 °C for 5 min, raised to 280 °C at a rate of 3 °C/min, and finally held at 280 °C for 5 min. The temperature interface of the GC-MS was kept at 250 °C and the mass spectrometer was operated in EI mode at 70 eV with *m/z* from 35 to 450. The chromatographic peaks were identified by comparison to the National Institute of Standards and Technology (NIST) library. Assuming that the response factor for each compound was the same, the concentration of compounds in the sample increases in linear manner with peak area percentage. The distribution of distillation range was also tested by simulated distillation using GC (Agilent 7890A) with a 0.5 m packed column and a FID detector. N-paraffins ranging from C5-C60 were used as standard substances for simulated distillation. Finally, FT-IR (Nexus 670, Nicolet Co.) was employed to study the organic functional groups of the feedstock and product.

2.3. Hydrotreatment procedure

The hydrotreatment of low temperature coal tar distillate was carried out in a hydrotreatment unit (Fig. 1). A commercially available catalyst, MoNiWP/Al₂O₃, was used in this study. The catalyst was first crushed and sieved through 20–40 mesh (0.42–0.84 mm). The fixed bed reactor with an inner diameter of 8 mm was firstly packed by sequence with 4 mL quartz sand placed, then 3 mL MoNiWP/Al₂O₃ catalyst, and finally 4 mL quartz sand. Before reaction, the catalyst in situ was presulfided at 360 °C for 4 h at 3 MPa. The presulfiding solution was 5 wt% carbon disulfide in cyclohexane. The flow rates of H₂ and presulfiding solution were 100 mL/min and 0.5 mL/min, respectively. After presulfiding, the temperature, pressure and liquid hourly space velocity (LHSV) were adjusted to the desired reaction values as follows. The reference reaction conditions were 375 °C, 6 MPa, LHSV of 1 h⁻¹, and H₂: oil ratio of 1500:1. Separate hydrotreatments were carried out under this constant H₂: oil ratio with temperature range between 325 and 400 °C, pressures between 3 and 7 MPa and LHSVs between 0.4 and 1.2 h⁻¹. Normally, one of these three variables was changed while the others were held under reference conditions. During each run, three samples were taken at intervals of 1 h, the first sample collected 4 h after initiating the reaction to ensure reaction conditions and catalyst activity were stable at the time of sampling.

3. Results and discussion

3.1. Feedstock composition

GC-MS was employed to identify the chemical components in both feedstock and product, and to calculate the contribution of each component to the overall composition. We identified up to 80 compounds constituting over 90% of the total sample using the NIST GC-MS spectral database. All the compounds identified are classified into ten groups based on saturation level and presence or absence of phenolic hydroxyl groups as follows:

1. Alkenes: alkenes with C13–C16.
2. Alkanes: alkanes with C12–C20.

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