



ESI FT-ICR mass spectral analysis of coal liquefaction products

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Abstract

We have applied electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to analyze the pyridine soluble fraction of a distillation resid and a further processed liquid product in a coal liquefaction process. The inherent high resolving power ($m/\Delta m_{50\%} > 300,000$, in which $\Delta m_{50\%}$ is full mass spectral peak width at half-maximum peak height) and mass accuracy (< 1 ppm) of FT-ICR MS makes it possible to resolve and identify polar heteroatomic species. The resid contains more heteroatomic compounds and a higher molecular weight distribution whereas the liquid sample is lower in average mass and more saturated. The data confirms that the liquefaction process produces lower mass, hydrogenated liquid product whereas the resid (highly aromatic and of high heteroatom content) must be recycled to reduce its heteroatom content and increase its degree of saturation.

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1. Introduction

Growing environmental problems associated with increased production and consumption of commercial fuels have led the USA Environmental Protection Agency (EPA) to establish progressively more stringent standards in an effort to reduce automobile emissions in the future. Both fuel type and quality have a major impact on the direct mobile source emission and performance of vehicle emission control technology. For example, EPA has announced plans to reduce sulfur in on-road diesel fuel by 97% by mid-2006 as well as hydrocarbons and nitrogen oxide emissions by 70% beyond the current standards for non-road small spark-ignition handheld engines. Therefore, advances in clean fuel technology are required to reduce heteroatom content (primarily nitrogen and sulfur) and improve the quality of commercial fuels. The petroleum industry has met the current standards by increasing

hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) capacity. The near-future standards and ultimately the quest for zero-sulfur fuels will certainly be met through further (deeper) HDS and HDN refinery processes or through more recent sorbent technology [1,2]. In any case, knowledge of the detailed chemical composition of the source material before and after processing will be invaluable for evaluating processing efficiency and optimizing reactor conditions. An analogous refinery process effort has previously been made to convert coal to liquid fuel. As for raw crude distillates from source crudes with high N and S content, the raw coal liquefaction product has high heteroatom content and consequently must undergo further treatment before yielding a commercial fuel [3].

Coal, the most abundant, widely distributed, and economical fossil fuel, is a solid with high carbon content but low hydrogen content (usually less than 6%). As a solid, coal is not easily used as a transportation fuel. However, transportation fuels and other chemicals may be derived from coal through liquefaction. The two methods to convert solid coal into liquid fuel are direct liquefaction and indirect liquefaction. Direct liquefaction, the most efficient route currently available, with catalyst and a hydrogen donor solvent at very high temperature and pressure, can convert coal into artificial petroleum. In indirect liquefaction, coal

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is completely gasified with steam. The gasification products are mixed with H₂ and CO with the removal of sulfur-containing species. Over a catalyst at relatively low pressure and temperature, the mixture reacts to produce the final synthesis liquid fuel. By adjusting the composition of catalyst, hydrogen/carbon ratio, temperature, pressure, etc., one can obtain a variety of different products, such as paraffins, olefinic hydrocarbons or alcohols [4].

The liquefaction rate and extent depend heavily on the temperature, pressure, and catalyst [5–12]. Diverse coal liquefaction procedures are tailored to the properties of the specific coal resource or desired final products: e.g. the solvent-refined coal (SRC) process was developed to produce cleaner boiler fuels; whereas the Canada Centre for Mineral and Energy Technology (CANMET) hydrocracking process is intended to co-process coal with petroleum bitumen for conversion into distillate products [13–17].

In addition to converting coal into liquid fuel, coal liquefaction necessarily removes heteroatomic compounds such as N-, S-, O-, and metal-containing compounds that contribute to fuel instability during storage [18,19] and to air pollution upon combustion by release of NO_x and SO_x gases [20,21]. Direct coal liquefaction is considered to take place in two consecutive steps: conversion to a soluble form and reduction in molecular weight and removal of heteroatoms by hydrodesulfurization and denitrogenation [22–26], known as the ‘upgrading’ process. Thus, it is important to monitor the fate of sulfur- and nitrogen-containing compounds during the coal liquefaction process. However, research has been hampered due to the lack of precise structural information on heteroatomic groups in coal [27–30]. Moreover, coal liquefaction processes involve complex multi-stage refining. The development and optimization of coal liquefaction requires a complete evaluation of not only the products but also the distribution of polar heteroatom-containing compounds throughout the entire process. Such detailed compositional information has hitherto either been unattainable (resid samples) or required months to complete (distillate samples) by GC-MS. Moreover, detailed compositional information relates to the end use of the coal-derived liquid. For example, for end use as a petroleum feedstock, characterization and hence separation of specific compounds such as phenols are necessary [31].

We have previously demonstrated electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) for analysis of Illinois #6 and Pocahontas #3 pyridine coal extracts [32]. ESI coupled to high-field (9.4 T) FT-ICR MS has resolved and identified elemental compositions (C_cH_hN_nO_oS_s) of up to literally thousands of NSO-containing compounds (observed as positive or negative molecular ions from basic or acidic species, respectively) in crude oils and their distillates [33–39]. Here, we extend the ESI FT-ICR MS method to detailed chemical compositional analysis of polar compounds in fractions isolated from different stages of

the coal liquefaction process. We are able to trace all of the heteroatomic species for two very different types of samples (distillation resid and distillation liquid) in the multi-stage complex refining process without any pre-chromatographic separation. This effort lays the groundwork for better understanding of the fate and/or modification of heteroatom containing polar species (solid and liquid) in multi-stage refinery processes such as coal liquefaction. The present example demonstrates the strength and flexibility of the technique and presages its extension to other industrial/refinery processes.

2. Experimental methods

The coal liquefaction samples were kindly provided by CONSOL Energy, Inc. (Pittsburgh, PA). The materials were all produced in 1996 in a single continuous bench-scale direct coal liquefaction unit run at Hydrocarbon Technologies, Inc. The feedstock to the run was sub-bituminous coal from the Black Thunder Mine (Wyoming). The early stage sample, PFL (pressure filter liquid) resid, period 19, corresponds to the distillation residue of the PFL stream taken during the 19th day of the process. The resid was produced from the recycled PFL stream by batch distillation to an endpoint of ~850 F. The final liquid sample, SOH, period 23, is the separator overhead (SOH) stream and the major net product of the process. It is a coal-derived substitute for petroleum distillate but not a fully refined consumer fuel. The liquefaction process has been described elsewhere [40,41].

2.1. Sample preparation

The resid sample is a dark solid and the liquid SOH sample is a yellowish liquid. Prior to ESI FT-ICR MS analysis, a solution of 10 mg of each sample was dissolved in 5 mL of pyridine. The pyridine solubles were decanted and then diluted with 15 mL of methanol. One milliliter of the solution mixture was removed and spiked with 10 μL of pure (99.9%) ammonium hydroxide. All solvents were HPLC grade (Fisher Scientific, Pittsburgh, PA).

2.2. Mass analysis

Mass analysis was performed with a homebuilt FT-ICR mass spectrometer equipped with a 22 cm diameter horizontal bore 9.4 T magnet (Oxford Corp., Oxney Mead, England) [42]. Data were collected and processed with a modular ICR data acquisition system (MIDAS) [43,44]. Negative ions were generated from a microelectrospray source equipped with a 50 μm i.d. fused silica micro ESI needle. Samples were infused at a flow rate of 400 nL/min. Typical ESI conditions were needle voltage, –1.8 kV; tube lens, –390 V; and heated capillary current, 4 A. Ions were accumulated external to the magnet [45] in

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