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Characterization of sulfur coal-derived liquids as a source of hydrocarbons to produce chemicals and synthetic fuels

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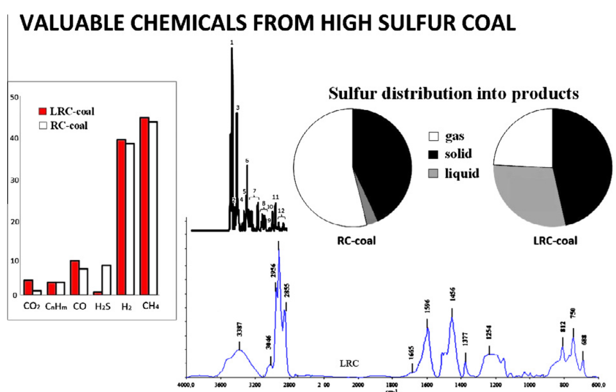
HIGHLIGHTS

- Effect of genetic type by reductivity on coal-derived liquids was established.
- General distribution of coal sulfur during mild pyrolysis was investigated.
- Quality and quantity of primary tars had similarity to the commercial motor fuels.
- High sulfur coal yielded liquids with low level of sulfur and undesirable compounds.
- High conversion ratio of low-quality coal into liquids and gases was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to foster an effective utilization of the high-sulfur coal reserves and promote a wide implementation of coal-to-liquid technologies, the behavior of two low rank bituminous coals with different *genetic type by reductivity* during mild pyrolysis process was investigated. The influence of the *genetic type by reductivity* on the formation mechanism of primary tar was studied. The final objective was to determine which coal yields more quality products and primary tar as alternative source of feedstocks to produce valuable chemicals and motor fuels. Qualitative and quantitative measurements of the liquid hydrocarbons and gas mixture obtained from coals were performed by MIR-spectrometry, ^{1}H NMR, a VTI-II gas analyzer and gas chromatography. Results demonstrated the influence of the *genetic type by reductivity* on the hydrogen-type distribution between the mild-pyrolysis products. It was shown that a high sulfur level in the original coal allows increasing the conversion ratios of organic matter into high-quality gaseous products with high concentration of H_2S and almost sulfur-free coal liquids.

1. Introduction

Increasing awareness of the scarcity of new crude oil reservoirs and unstable crude oil prices, as well as concerns around security of supply and sustainable development have increased the interest in the diversification of a country's oil supply; in particular, the production of alternative liquid fuels from coal [1]. In this regard, primary tar (the hydrocarbons mixture obtained from coal) can be considered a competitive, economically feasible source of liquid hydrocarbons to produce valuable chemicals and to supplement or to replace traditional petroleum-based supplies of high-quality motor fuels.

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Ukraine's coal endowment outstands in Europe (85.8 Mt extracted in 2012), only after Russia and Germany. In 2007, it was reported that coal reservoirs amount in excess 45,164 million tonnes, of which 45% ranked as bituminous, 49% as sub-bituminous and about 6% as lignite [2]. This would support current levels of coal production in the country for more than 390 years. However, most coal seams are very deep (1000–1800 m depth) and are thin (ca. 0.6–2.5 m thickness) [3]. Despite about 570 coal seams are considered mineable in the Donetsk coal Basin, 73.6% of them are predominantly low-quality coals with high (>2.5 wt%) sulfur contents. Thus, scarcity of high-quality coals forces the use of low-rank coals with high content of sulfur. Unfortunately, the high level of sulfur in Ukrainian coals causes environmental and technological problems during their utilization [4].

The differences in the physicochemical, thermochemical and geochemical characteristics of the coals are due to the structural features of the organic matrix and specific depositional environments (peat-formation period and coalification), including the degree of decomposition of the plant residues during early diagenesis processes [5,6]. The Donetsk coal basin was formed in an alluvial or marine depositional environment resulting in a range of marine and terrestrial inputs. The coal seams created through the inputs of marine transgressions dominate the Donetsk coal basin [7]. The formation of these coals occurred under a more reductive environment with sea water and the presence of anaerobic bacteria. Coals formed under less reductive conditions implied a freshwater environment, nourishing peat-land, whose burial was accomplished by fluvial sediments [8].

It has been established that Donetsk low- and high-sulfur coals of the same coal rank are significantly different in terms of their coal properties depending on the *genetic type by reductivity* [9]. This parameter was suggested as a fundamental characteristic of coal deposits to improve current coal classification systems [10]. The effects of the *genetic type by reductivity* of coal on the yield of fluid non-volatile products and on the character of the chemical interactions during formation of plastic layer have been studied elsewhere [11].

Coal liquids can be produced using four major coal-to-liquid processes: pyrolysis (mild pyrolysis, flash pyrolysis and hydropyrolysis), solvent extraction (using a non-hydrogen-donor solvent), direct coal liquefaction (DCL, single-stage and two-stage processes) and indirect coal liquefaction (ICL, Fischer-Tropsch's synthesis) [12,13]. However, not all these technologies have reached commercial maturity, and many are at a precommercial stage. Relevant exceptions are the Sasol's Advanced Synthol High-Temperature Fischer-Tropsch (FT) synthesis plant; the Sasol's Slurry Phase Distillate Low-Temperature FT-synthesis process and the world's first DCL commercial plant in the Inner Mongolia Autonomous Region of China [14,15].

All coal-to-liquid technologies differ significantly in terms of their complexity, although they share prohibitively high market entrance prices, large capital costs at their initial implementation phase and significantly high margin between entrance and shut-down prices [1]. Most successful commercial enterprises producing liquid fuels from coal are largely based on ICL processes [16]. Moreover, large-scale applications of ICL have been done in regions where open-cut mining was possible. Considering the complex geological characteristics of the Donetsk coal basin (underground mining, high depth and thin coal seams), profitability of the production of liquid hydrocarbons and gaseous fuels from coal using ICL can be questioned.

In this regard, the development and implementation of a highly efficient cleaning coal technology is a must for coal-producing countries. Such a technology should allow for increasing the conversion ratios of solid feedstock into valuable chemicals and alleviating environmental impacts.

Obviously, selecting a coal technology is primarily based on evaluating the composition and properties of the raw material and the expected products. Several researchers reported on some parent coal characteristics which have an influence on the chemical composition and properties of low-temperature primary tar [17,18]. It was found that the yield of primary coal tar is a function of the coal rank [19]. A relationship between the chemical composition of primary tar and the effect of coal rank, maceral composition and thermal behavior has been established [20]. Also, a relationship between the composition of low-temperature tar and the coking pressure has been investigated [21]. Recently the maximum temperature of thermal decomposition (T_{max}) of the parent coal and the yield of pyrolysis tar have been related [22]. It was reported that low-temperature pyrolysis of low-quality coals at T_{max} increases the quantity of the major products, as carbon residue and primary tar [23]. Also, a novel integrated process was introduced to improve the yield of low-temperature tar as much as 32 wt% when compared with traditional pyrolysis processes [24].

Primary coal tar constitutes a source of hydrocarbons for the fuel industry and the chemistry of raw materials [25,26]. This complex mixture includes tens of thousands of organic compounds with different functional groups and has a broad molecular-weight distribution [27]. Primary tar is considered a valuable feedstock to produce engineered plastics, new carbon materials, high-temperature endurable insulating materials, synthetic waxes, lubricants, defense materials and drugs. In addition, coal liquids contain polynuclear hydrocarbons, which cannot be obtained from crude oil [28].

The quality and quantity of coal liquids depend on some major factors: (1) the chemical nature and structure of the coal organic matter; (2) the thermochemical characteristics of the original coals; (3) the operational conditions (heating rate, final temperature, pyrolysis atmosphere and pressure) and (4) the reactor design.

As is well known, production of primary tar provides an additional economic benefit to a coal pyrolysis process. According to [29] mild pyrolysis and subsequent hydrogenation of primary tar may lead to thermal efficiencies of around 85%. Considering the valuable products such as primary tar, pyrolysis gas and semicoke, the profitability of this production is possible.

The formation mechanism of liquids obtained during thermal decomposition of coal is known in coal chemistry. The re-distribution of the available hydrogen occurs via a sequence of free radical mechanism (including hydrogen abstraction, disproportionation, and beta-bond scission). However, the specific (particular) reactions are still the subject of discussion. For example, according to the molecular model of coal structure suggested by Marzec, the so-called mobile phase in the coal organic matter consists of donors as well as acceptors of hydrogen [30,31]. Under pyrolysis conditions, under atmosphere of evolving gases (permanent and condensable) radical reactions occur via two competitive directions: on the one hand, recombination with formation of a solid phase (semicoke) and on the other hand, stabilization of radicals with formation of a liquid products.

Coal pyrolysis of different coking coal ranks has been studied in detail. However, the behavior of coals with different *genetic type by reductivity* during mild pyrolysis process was not described exactly. The influence of the *genetic type by reductivity* on the formation mechanism of primary tar during coal pyrolysis is still unknown.

The major aim of the present research is to establish the effect of the *genetic type by reductivity* on the qualitative and quantitative characteristics of primary coal pyrolysis products. This was accomplished by studying the structure and properties of low-rank bituminous coals distinguished by their sulfur content, retrieving