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Production and characterization of ash-free coal from low-rank Canadian coal by solvent extraction

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ABSTRACT

In this work, ash-free coal (AFC) was extracted from low-rank Canadian coals with mean maximum vitrinite reflectance (MMVR) in the range of 0.38–0.69 using non-polar organic solvent, organic solvent combination (polar–nonpolar solvent mixture), and with and without hydro-treated heavy aromatic hydrocarbon solvents from coal–tar industry to study the effect of type of coal and solvent type on the production yield of AFC. High temperature solvent extraction was carried out in 0.5 L autoclave in the temperature range of 473 to 723 K. It was observed that 1-methylnaphthalene (1-MN), a non-polar solvent did not give any significant difference in yields [~30% (daf)]. However, an extraction yield of 73% (daf) AFC was achieved using hydrotreated aromatic hydrocarbons at 673 K. The performance of extraction yields was correlated by the vitrinite content and MMVR of the coal and it was observed that higher proportions of vitrinite and a lower MMVR value of coal produced higher extraction yield. Proximate and ultimate analysis, FTIR, ICP-MS, ^{13}C CP/MAS NMR, thermogravimetric analysis and particle size distribution were used to characterize AFC. The heating value of the AFC was estimated to be in the range of 36–37 MJ/kg and a substantial decrease of sulfur content (ca. 12.5–61.1%) is also observed in AFC. AFC showed a narrower particle size distribution with a d_{50} of 7.0 μm.

1. Introduction

The natural abundance of coal reserves and its low cost-effective availability are increasing the demand of coals and its utilization to produce energy and liquid fuels. There is a recent need in using low-rank coals, such as lignite and sub-bituminous, because of the increased demand of power and other applications. However, these coals have several limitations, such as higher mineral matter and moisture contents and low calorific value. Moreover, the utilization of such coals aggravates various environmental problems, such as SO_x emission and high GHG emissions. It is also necessary to remove the mineral matter from coal to be combusted directly in the new generation integrated gas combined cycle (IGCC) gas turbines to overcome issues like erosion and corrosion of turbine blade and fouling due to coal ash deposition. Thus, it is advantageous to upgrade coals in terms of mineral mater and moisture content. A new cost-effective and efficient process is therefore essential to remove the mineral matter and upgrade the low-rank lignite and sub-bituminous coals. One such technology could be the production of ash-free coal (AFC). It could be a preferred feed for some applications, such as direct combustion in the gas turbines [1]. Utilization of AFC directly in a gas turbine as fuel can generate a power system of higher thermal efficiency without damaging the turbine blades [1,2].

There are two main types of chemical upgrading of coals to produce clean coal. The first one, aiming to produce the upgraded coal using strong acids or alkalis to dissolve all the minerals leaving the organic coal matrix under hydrothermal conditions [3–6], is termed as UCC. The second process uses organic solvents to dissolve organic matter and precipitating back the ash free coal known as hyper-coal [1,7,8]. It is termed here as ash free coal (AFC). However, the coal from the UCC process may contain around 0.5% ash [7,8] and cannot be directly fired in the gas turbines. Another possible concern could be associated with the corrosiveness and biodegradability of strong acids and alkali reagents used and consequently disposal of the waste solution. On the other hand, solvent extraction of coal using organic solvents can produce AFC that has significantly much lower ash content than that obtained from UCC process. Besides, this process helps to remove alkali and heavy metals and almost all inorganic sulfurs. However, there are some limitations of the ash free coal preparation process, such as low product yield and use of residual coal discharged. A subsequent process is still needed to reduce alkali metal (Na and K) contents to less than 0.5 ppm, which is the current acceptable level for introduction to gas turbine [9]. But, since the residual coal with high ash content contains no moisture and it has high heat value, they can be utilized effectively for power generation or steam generation using fluidized bed combustors. The residue coals also have high reactivity and can be used as reducing agent in the synthetic rutile production from ilmenite resources [10]. Therefore, continuous research efforts are being made to identify the coal and solvent, in particular, low-cost industrial solvent to maximize the extraction yield and reducing the amount of residual coal.

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1.1. Literature review

A number of solvents like, polar, non-polar and mixture of solvents have been used for the solvent extraction of coal for the production of AFC [1,7,11–15]. It is postulated that high temperature solvent extraction of coal is driven by the affinity of organic moieties of coal matrix to an organic solvent. Consequently, coal–solvent interaction dissociates and disrupts both the covalent and non-covalent interactions (hydrogen bonds, van der Waals interactions, electrostatic interactions and π–π interactions) in coal molecules [12,16–18]. It has been also observed that extraction yield not only depends on the rank of the coal but also on the solvent type as well as on extraction temperature [12–14].

N-Methyl-2-pyrrolidinone (NMP), a polar aprotic solvent has been extensively used under widely varying conditions for the extraction of coal [14,19–22]. A number of studies describe its use alone [19] and in combination with other solvents such as carbon disulfide (CS_2) [23–25]. Renganathan et al. [19] investigated extraction of various bituminous coals at 475 K using NMP to reduce the ash and pyritic sulfur. Kim et al. [14] also used NMP to produce low ash coal from low rank coals and observed that the extraction yield increases with the increase of extraction temperature, and the ash content of extracted coal decrease below 0.4% at 673 K from the raw coal samples that have the ash content in the range of 4–6%. Cai et al. [20], White et al. [21] and Seehra et al. [22] reported that NMP reacts with coal particles when extraction was carried out at its boiling point under nitrogen atmosphere and breaks the carbon–oxygen bonds. Extraction yield was further improved through the addition of a variety of additives into NMP solvent. Iino et al. [23] reported a high extraction yield (45–78%, daf) at room temperature for bituminous coals using a binary solvent system CS_2/NMP. The CS_2/NMP mixed solvent has a synergistic effect and often extracts significantly more material from coals than the more commonly used pyridine [23,24]. Ishizuka and co-worker [26] reported an extraction yield of 84.6% with a tertiary solvent system CS_2/NMP/tetracyanoethylene. Ouchi et al. [27] studied thermal extraction of a Japanese bituminous coal using pyridine and quinoline in an autoclave under 1 MPa of nitrogen pressure at 473–673 K. They reported an extraction yield of 50 wt.% at 673 K with pyridine and a similar extraction yield using quinoline at 573 K. The maximum yield achieved was about 80% with quinoline at 623 K. In view of the above, polar aprotic solvent provides higher extraction yield irrespective of coal type. However, it has been reported that during coal extraction with NMP, a large amount of NMP was lost due to a strong linkage with coal molecules [20,28,29].

Solvent extraction of coal using nonpolar solvents such as tetralin and 1-methylnaphthalene (1-MN), and dimethylnaphthalene (DMN) has also been investigated to produce AFC. Miura et al. [30] conducted extraction of Argonne premium coals and an Australian brown coal in a flowing stream of nonpolar solvents such as tetralin and 1-MN at 473–673 K and 10 MPa pressure and observed that the bituminous coals have shown negligible decomposition below 623 K and obtained yield of 65–80% at 623 K. Yoshida et al. [7] studied solvent extraction with organic solvents such as tetralin, 1-MN, and DMN for various ranks of coals at 473–653 K using a batch extractor under inert atmosphere. Extraction yield was 24–54% with DMN at 633 K and was independent of coal rank. Okuyama et al. [1] investigated 20 different coals of Chinese origin, mainly bituminous and extracted with 1-MN and tetralin. The extraction yields were within the range 30–70% at 633 K and these yields were largely dependent on the coal characteristics. They also observed that the extraction performance of tetralin was better than that of 1-MN. This may be due to the presence of hydrogen donor capability of tetralin. However, they reported that a part of tetralin was changed to naphthalene by hydrogen transfer to coal during extraction process [29].

More recently, solvent extraction of coal has also been carried out utilizing mixed solvents and industrial solvents, such as light cycle oil (LCO), carbol oil, and crude methylnaphthalene oil (CMNO). LCO, a non-polar by-product obtained from cracking of vacuum gas oil to produce gasoline is composed of mainly two or three aromatic ring compounds. Carbol oil is a coal tar distillate composed of mainly phenolic derivatives. Whereas, CMNO another coal tar distillate, is composed of mainly 1-MN together with naphthalene, DMN and acenaphthilene, quinoline, isoquinoline, indoles etc. [31]. Yoshida et al. [7,31] performed production of ash-less coal with LCO and CMNO under hot filtration at 633 K using a flow-type extractor. They reported higher extraction yield for CMNO (~81%) than LCO (~63%). It is interpreted that high extraction yield obtained due to the solvent-induced relaxation of coal aggregates by the nitrogen-containing compounds, in addition to the thermal-induced relaxation of them. However, they could not establish the relation between the yields obtained and coal type with LCO. Yoshida et al. [31] also investigated the effect of addition of some polar compounds into non-polar extraction solvent on the extraction yield. They observed that the extraction yield increases linearly with the increase of polar components. However, the extraction yield could not reach as high as the extraction yield obtained with CMNO itself used as solvent. Masaki et al. [12] reported that acid pretreatment could increase the extraction yield for sub-bituminous coal using CMNO and also observed that enhancement in extraction yield due to the addition of 20% NMP in CMNO. Miura et al. [32] reported extraction yield of nearly 80% at 623 K for in sub-bituminous and brown coal using carbol oil solvent.

The influence of the maceral type and their content on the technological conversion of coal is also being studied by various research groups [33]. It is also important to understand the maceral transition during solvent extraction process. The performance of coal liquefaction has been evaluated using petrographic methods. Refs. [18,33–36] studied the reactivity of the inertinite and vitrinite-rich coals with different organic solvents and observed that the extraction yield was lower for inertinite-rich coals. Recently, Niekerk et al. [18] studied on South African coals of similar rank with the different maceral content and found a relationship between the extraction yields and mean maximum reflectance (MMVR). They indicated that the higher the MMVR of the coal lower the extraction yield.

From the foregoing discussion, it is found that most of the works on thermal extraction of coal to produce AFC, have been performed using bituminous and sub-bituminous coals from the Australian, Indonesian, South African and American origins [7,13,17,30,32,37,38]. However, in spite of abundant availability of low-rank coal (LRC) in Canada, there was no study available in literature for preparation of AFC using industrial solvents, such as heavy aromatic hydrocarbons and hydrotreated heavy aromatic hydrocarbons. Therefore, these coals are selected as they are the most likely coals to be used by the Canadian coal industries. It is also hypothesized in this work that the maceral composition in coal plays a significant role on AFC yield. However, in spite of its immense importance, literature on the effect of maceral component on extraction yield of AFC is scarce. Therefore, one of the objectives of this study is to investigate the effect of vitrinite and/or inertinite content of the LRCs on AFC yield and to establish a relationship between the mean maximum vitrinite reflectance of the raw coal with the extraction yield of AFC.

Type of solvent plays a vital role in extraction of AFC. The use of inexpensive industrial solvent in AFC production process is of increasing interest today. The use of these solvents can bring about a significant improvement in the AFC yield and quality of AFC and a great saving in solvent reclamation cost. Although, there are a few investigation available with the industrial solvent like CMNO and LCO, but there are no literature available for the hydrotreated industrial solvents. It was, therefore, thought desirable to undertake this work to investigate the effect of this new kind of solvent on the extraction yield of AFC and to study the role of heavy aromatic hydrocarbons present in the hydrotreated industrial solvents.

Knowledge of some fundamental physicochemical property data, such as trace element present, types of aromatic/aliphatic carbon percentage distribution, particle size distribution and heating value of AFC produced are essential to determine its quality as well as for the