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Beneficiation of Coals: A Review

Shashwata Ghosh *, Dr. Chanchal Mondal
* Chemical Engineering Department, Jadavpur University, India
sashwata0910@gmail.com

Abstract

Coal is an important fossil fuel and is used as a major source of energy in power plants and blast furnaces. But, Indian coals contain a large amount of impurities, particularly ash forming mineral matter, which interfere with proper combustion of coal and decreases its calorific value. Industrial uses demand coal with minimum ash content so that it can be efficiently used in metallurgical, or, power plants. This paper reviews the removal of ash-forming minerals of coal using chemical techniques and also the extraction of coal by the use of various solvents. Solvents, like N-Methyl-2-pyrrolidone (NMP), 1-methyl naphthalene, Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO) can be used to reduce the ash content of coal. However, polar solvents have been proved to extract greater amounts of coal and reduce ash to a greater extent than non-polar solvents, particularly for lower rank, or, sub-bituminous coals. However, if non-polar solvents are used, then traces of polar additives can also increase the extraction of coal as well as cause greater reduction of the ash content. The degree of ash reduction not only depends on the solvent used, but also on the extraction temperature, time and rank of coal.

Keywords: coal, ash, minerals, solvents, rank of coal, extraction

Introduction

Coal is an important source of energy and is used in many industries like coal-fired thermal power plants. Coal is also converted into coke, which is used as a fuel as well as a reducing agent in smelting iron ore in a blast furnace. But the presence of a high percentage of ash-forming minerals in coal is disadvantageous. These minerals are converted into ash during combustion of coal. These are inherent mineral matter and Indian coals consist of high percentage of such minerals. The mineral matter mainly consists of aluminosilicates apart from pyrites and few other compounds. The presence of high ash not only interfere with the effective utilization of coals due to heat losses, but the disposal of large amounts of ash is also a problem.

Many studies have been conducted to reduce the ash content of coal by the use of various solvents. Studies have also been made to increase the percentage of coal extracted. The effects of various parameters like temperature, pressure, effects of additives, etc. have been studied. The main aim of this review is to determine the various parameters which decrease the ash content of coal as well as increase the extraction of coal. The effects of the various chemicals used in these studies provide important clues as to how ash content of coal can be reduced to a significantly low percentage.

Coal beneficiation by chemical treatment

Coal beneficiation by agglomeration techniques

Beneficiation of bituminous and lignite coals can be done by agglomeration using binding oils containing either p-xylene, or deodorized rectisol naphtha and the reduction in ash content has been studied with respect to particle size, mixing speed, mixing time, oil to coal ratio and oil characteristics. It has been observed that the ash reduction of 320 mesh bituminous coal was more than that of 200 mesh coal showing reductions of 17% and 14%, respectively (Timpe et al.). Thus, the ash reduction of smaller sized particles is greater than that of the larger ones. Higher mixing speeds and longer mixing times has been reported to have removed greater percentage of ash, but smaller flocs are formed, which are difficult to handle. Hot water dried lignite shows greater removal of ash compared to as received lignite (Timpe et al.). However, this method does not remove ash to a much larger extent as done by other chemicals.

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Rank of coal in relation to extraction

For higher rank Bituminous coals, it has been observed that the extraction yields increase with an increase in temperature and there is a peak temperature at which a maximum extraction yield is obtained. Beyond this peak temperature, the extraction rate again drops. This is related to the thermal relaxation of molecules. At the peak temperatures, relatively small molecules may be released from the cross-linking coal structure to the solvent (Okuyama et al., 2004).

For lower rank coals, like sub-bituminous and lignite coals, the extraction yield has been observed to increase with increase in temperature. A suitable solvent and high temperature of about 673K gives an extraction yield of over 70% and very low, or, negligible ash content (Rahman et al., 2013), as shown in figure 1. In figure 1, BD, BL and POP are lignite coals, while CV and GEN are sub-bituminous coals. A higher proportion of vitrinite and lower value of MMVR (mean maximum vitrinite reflectance) has been reported to have given higher extraction yield as lower MMVR values signify higher reactivity of coal (Rahman et al., 2013).

Figure:

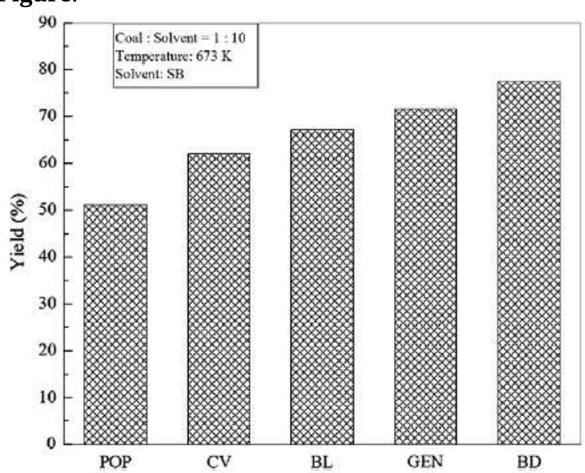

Fig. 1: Effect of coal type on extraction yield using hydrotreated solvent SB with 1 h of holding time at 673 K. (Rahman et al., 2013)

Effect of temperature and pressure on extraction of coal

For higher rank coals, like Bituminous coals, it has been observed that the extraction yields increase with an increase in temperature and there is a peak temperature at which a maximum extraction yield is obtained, as shown in figure 2. Beyond this peak temperature, the extraction rate again drops. The peak temperature at which the extraction yield becomes maximum has been related to the softening temperature of coal. When the coal softening point is closer and closer to the extraction temperature, the coal extraction becomes higher and higher (Okuyama et al., 2004). At the softening point, the structure becomes relaxed and beyond the softening point, the coal is restructured by cross-linking, which results in a decrease in extraction yield (Kim et al., 2007). This is possibly due to the enhanced coal–solvent interaction at this temperature and consequently, higher solvent induced thermal relaxation of coal molecules is occurring and releasing mainly small molecules and free radicals from the cross-linking coal structure to the solvent (Okuyama et al., 2004). In figure 2, Kideko and Roto south are sub-bituinous coals, while Sunhwa is a Bituminous coal (Kim et al., 2007).

Figure:

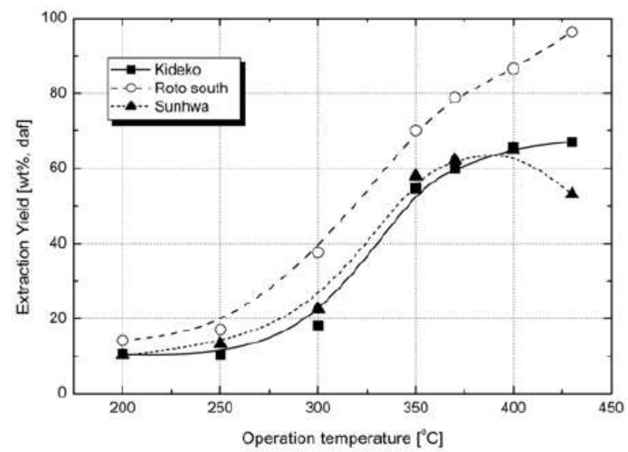

Fig. 2: Variation of extraction yield with temperature (Kim et al., 2007)

For lower rank coals, such as lignite and sub-bituminous coals, there is no softening temperature at which the coal structure becomes relaxed and so a polar solvent is required to breakdown the structure (Kim et al., 2007).

The ash content of coal extracts from both Bituminous as well as sub-bituminous coals decrease as the extraction temperature increases (Kim et al., 2007).

The initial applied pressure has no significant effect on the extraction yield and ash reduction; the extraction yield and ash reduction can be enhanced more by increasing extraction temperature rather than the initial pressure (Kim et al., 2007), as shown in figure 3.

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Figure:

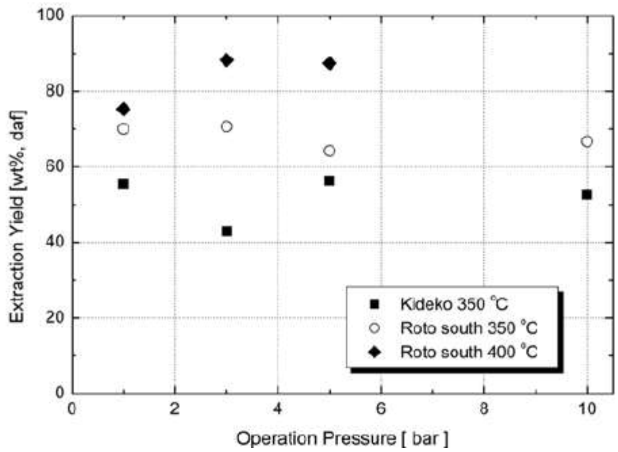

Fig. 3: Variation of extraction yield with initial applied pressure (Kim et al., 2007)

Effect of polar and non-polar solvents on extraction of coal

For higher rank coals, like Bituminous coals, it has been reported that non-polar aprotic solvents like 1-methylnaphthalene can give satisfactory yields of about 70% by weight (daf) and ash content reduced to several hundreds of ppm at 340-360℃ (Okuyama et al., 2004). However, it has also been observed that if a hydrogen donating solvent like tetralin is used, the extraction rate becomes more than that obtained when an aprotic solvent like the former is used at the same extraction temperature. This has been attributed to intermolecular hydrogen transfer from the solvent to the coal to stabilize small thermally decomposed molecules from coal and coal-softening phenomenon brings about this process (Okuyama et al., 2004). Polar solvents, like NMP have been reported to have given extraction yields of above 60% for Bituminous coals at temperatures above 350℃ (Kim et al., 2007).

However, in case of lower rank coals, such as lignite and sub-bituminous coals, there is no softening temperature at which the coal structure becomes relaxed and so a polar solvent is required to breakdown the structure (Kim et al., 2007). In case of sub-bituminous coals, it has been observed a polar solvent like NMP can give an extraction yield of over 80% at a temperature of about 400℃ (Kim et al., 2007). Hydrotreated aromatic hydrocarbons have given higher extraction yields for low rank coals than 1-methyl naphthalene because the latter contains polar components (Rahman et al., 2013). NMP has been reported a better solvent than non-polar ones for the low rank coals which have much of polar sites (Li et al., 2000).

Beneficiation by the use of inorganic chemicals

Beneficiation of Bituminous coals has also been done with aqueous HF followed by HNO_3 at temperatures of about 65℃. It has been observed that HF, if used alone reduces the ash content to about 2.6% by weight, while further treatment with HNO_3 reduced the ash content to about 0.6% by weight (Steel-Patrick, 2001). It was reported that prior to treatment with HNO_3, compounds such as AlF_3, $NaAlF_4$, CaF_2, MgF_2 formed during leaching and pyrites (FeS_2) does not react with HF. If HNO_3 is used, then the fluoride ions react with the H^+ ion of HNO_3 to form HF. However, HNO_3 only reacts with pyrites above a particular HNO_3 concentration, which suggests that it reacts with the organic coal structure to a certain extent (Steel-Patrick, 2001). Some amount of sulphur in the coal has also been observed to have decreased.

Effect of hot filtration and room temperature filtration on extraction

Coals of various ranks have been extracted with a variety of organic solvents, viz tetralin, 1-methyl naphthalene, dimethyl naphthalene and light cycle oil (LCO), which is a by-product of cracking of vacuum gas oil to gasoline. It has been observed that high extraction yields can be obtained if a suitably high extraction temperature is maintained; but, if the separation of residue and solution is conducted at room temperature, the extraction yields will not achieve the required specification of Hyper-coal.

Figure:

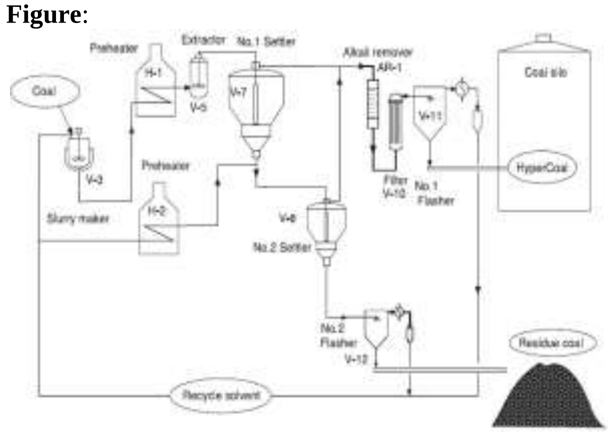

Fig. 4: Flow diagram of the Hyper-coal process (Okuyama et al., 2004)

The term Hyper-coal refers to ash-free coal (Okuyama et al., 2004). This has been attributed to the separation conducted at room temperature as the extract components soluble at high temperature might have deposited while quenching and decreased the percentage of coal extract (Yoshida et al., 2001). Hence, filtration after extraction should be performed

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at a high temperature in order to maintain a satisfactory extraction yield.

Beneficiation by mixtures of solvents

Beneficiation of coal by mixtures of solvent, like CS_2:NMP (in the ratio 1:1) has been reported to have given a higher extraction yield than that obtained when NMP is used alone. NMP is a polar solvent, but when CS_2 is added, a synergistic effect is obtained. It has been reported that with the CS_2 addition, the viscosity of the solvent mixture decreases and the ability of the mixed solvent to penetrate the cross-link coal structure increases, so that the mixed solvent can interact with the solvent-soluble molecules, such that the extraction yield increases (Shui et al., 2004). Large synergistic effects have been observed for coals used with NMP/HHA (1,4,5,8,9,10-Hexahydroanthracene) mixed solvents and using the mixed solvents, the dissolution yields increased, the extent of synergistic effect being highly dependent on the kind of coal used (Li et al., 2000). It has been reported that hydrogen donation from HHA to the coal coal radicals is the key reaction (Li et al., 2000).

Effect of various additives

It has been observed that addition of strong bases, like NaOH, or, sodium tertiary butoxide can increase the degree of dissolution of coal in solvents like NMP, DMF, etc. Depending on the extraction conditions, carbon extraction efficiencies of up to 90% have been obtained, (Makgato et al., 2008) as shown in figure 5. Sodium, or, potassium hydroxide is added as a solution with water. However, the addition of water has been observed to be detrimental for DMF due to base catalysed hydrolysis of DMF to dimethyl amine and formic acid in presence of water. Addition of sodium sulfide addition has been observed to have further reduced the ash content of the extracted coal. It has also been reported that as the NaOH/Na_2S molar ratio became high, the coal extraction also increased (Makgato et al., 2008).

The addition of a small amount of polar compound such as methanol to nitrogen-containing polar solvent has been observed to have greatly increased the thermal extraction yield for sub-bituminous coals at 360℃ (Kashimura et al., 2006).

Addition of salts like lithium and tetrabutylammonium salts with various anions to polar aprotic solvents, or, solvent mixtures have also been observed to have increased the extraction yield for several coals. The yields increase in the order $F^- > Cl^- > Br^- > I^-$, implying that smaller ions with large electronegativity are responsible for increase in yields. Hard bases like F^- & Cl^- attract proton and since, the solvent is polar and aprotic, these anions will not be solvated and can interact with some hard acidic sites in the coal (Takahashi, 2001). However, soft bases, like Br^- & I^- get solvated in the soft acid like CS_2-NMP mixture and cannot interact with the coal (Takahashi, 2001). It has also been reported that hard bases, like acetate ion can increase the extraction yield. It has also been reorted that the addition of alkali metal salts, like LiCl can increase the polarity of the solvents-salt solutions and increase the extraction of coal.

It has been observed that if the polar components of an industrial solvent like CMNO (crude methyl naphthalene oil) be separated, The extraction yields obtained with the extracted polar materials are 20-30% higher than that with CMNO (Kashimura et al., 2006). It has been reported that the major polar component of CMNO was quinoline and the minor constituents were isoquinoline, indole and methylquinoline. It has also been observed that indole has a greater ability to extract coal constituents compared to quinoline. But if both are used with a non-polar solvent, then a higher extraction yield compared to quinoline-nonpolar solvent mixture is obtained (Kashimura et al., 2006**)**.

Figure:

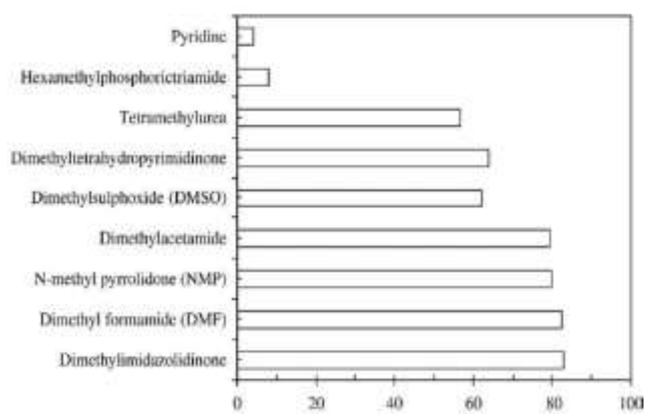

Fig. 5: The effect of solvent nature on the extraction efficiency at ambient conditions. Solvent:coal:KOH=100:10:1.56 on a mass basis. (Makgato et al., 2008)

Conclusion

Ash in coal and can be successfully reduced to a much lesser quantity by the use of proper solvents. Both polar and non-polar solvents can be used for the extraction of higher rank Bituminous coals. But for lower rank coals, like lignite, or, sub-bituminous coals, polar solvents are required to break down the structure for greater dissolution of coal.

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The extent of coal dissolution depends not only on the nature of solvent, but also on the rank of coal used, the extraction temperature and extraction time. The extraction temperature is again related to the softening temperature in case of Bituminous coals. But for lower rank coals, the extraction is not related to the softening temperature; extraction yield increases with increasing temperature, but a polar solvent is required to breakdown the structure. Pressure alone has no influence in the percentage of coal extracted, or, percentage of ash removed.

The filtration of residue and extract after extraction should be performed at a high temperature near the extraction temperature to ensure a high extraction yield, otherwise components soluble at a high temperature may be deposited while quenching at lower temperature.

The addition of certain additives, like polar compounds can increase the extraction yield from the coal. Addition of salts may also increase the percentage of ash removed by reacting with the inorganic compounds present in the coal and the products formed during rection may be precipitated, thereby decreasing the ash content of the extracted coal.

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Author Biblography

Shashwata Ghosh

Shahshwata Ghosh is a student of Master of Engineering (M.E.) in Chemical Engineering at Jadavpur University, Kolkata.
Email: sashwata0910@gmail.com

Dr. Chanchal Mondal

Dr. Chanchal Mondal is an Associate Professor, Department of Chemical Engineering, Jadavpur University, Kolkata.