

## Review on Beneficiation of Indian Coal Using Solvents

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**Abstract :** It is well known that Coal is an important fossil fuel and is used as a major source of energy in power plants and blast furnaces, but minerals in coal inhibit the effective utilization of coals. These are kind of troublesome materials in the combustors by forming the ash during combustion of coal. Industrial demand of coal with minimum ash content so that it can be efficiently used in metallurgical process, or, power plants. This paper reviews the removal of ash-forming minerals of coal using solvents by chemical techniques. Solvents, like N-Methyl-2-pyrrolidone (NMP), 1-methyl naphthalene (MN), 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 depends not only on the solvent used, but also on the extraction temperature, time and rank of coals.

**Keywords:** Coal rank; Ash-less coal; Mild condition; Binding oil; Cost-effective solvent; Thermal extraction.

### Introduction

As we enter the 21<sup>st</sup> century need for clean and efficient utilisation of coal is felt increasingly. This century coal is the heart in energy field. Finding new more efficient methods of beneficiation of higher ash coals has become a priority in coal research, as there are various potential uses of coal, as a fuel and non-fuel both (Shui et al.). Even coal can serve as a feedstock for aromatic chemical and carbon material such as graphite, carbon-fibres (Schobert, H.H et al.). Coal is also converted into coke, which can be used as a fuel & reducing agent. Coal is considered as major source of energy in power plants and blast furnaces due to its abundant deposit which is much higher in amounts (three times) than petroleum and its concern about energy security (lee et al.). Thus developing new, more effective process of beneficiation for higher ash coals has become a priority in coal research. But coal utilization has some limitation because production of large CO<sub>2</sub>, one of the major global warming gases (Mashimo et al.). However, a few years ago with the crisis of liquid fuel and hike in oil prices, the interest in purification of coal to utilize it as an alternative form of energy increases (Saito et al.).

Since coal have combustible hydrocarbons along with approximately 10% inorganic components called as “Mineral Matter”. These minerals in coal also inhibit its effective utilization. These mineral matter are kind of troublesome materials in the combustor by forming the ash during

combustion of coal and it creates various problems such as erosion of turbine blades, fouling on reboiler’s wall and tubes (Woo et al.). Although, the solution for such problems has been attempted. There are two methods to discard this mineral matter, Such as Leaching out of mineral matter from coal using alkali compound. This method was developed in USA and Australia, this process called as ‘UCC’ process (ultra clean coal) (Besida et al.). But exit effluent of this process containing 0.5% organic components which is undesired for direct use into gas turbine (Steel et al.). Another way is to remove organic components (as carbonaceous part of coal) by the use of solvent that behave as a catalyst, this process is called as “Hypercoal” process which developed in Japan. This process has aimed to produce ash free coal with a mineral matter amount lower than 0.02% so that this clean coal can be used directly into gas turbine (Kashimura et al., takanohashi et al.).

Particularly, this hypercoal process to produce ash free coal from low rank coal like lignite and sub-bituminous which are as abundant as bituminous coal but not used to large extent cause of high moisture content and low calorific value (Fujita et al.). Organic components from coal can be extracted using organic solvent like NMP (N-methyl-2-pyrrolidinone) which is a powerful solvent for coal extraction process, However, extraction yield is quite low at room temperature (Sakanishi et al). it is recommended to produce an ash-less coal by use of organic solvent extraction under sufficient high temperature but in absence of hydrogen atmosphere. Some specification (as shown in table-1) with comparison to SRC (solvent refined coal) in order to produce more than 60% extraction yield and ash content in hypercoal is less than 0.02%. The coal achieved after this process is in powder like raw coal, not pitch-like material (Yoshida et al).

Required specification for “Hyper-Coal”(Yoshida et al.).

	Hyper Coal	SRC
Temperature (°C)	<400	400-450
Pressure (gas)	Low (N <sub>2</sub> )	High (H <sub>2</sub> )
Extraction Yield (%)	>60	>60
Ash in Extract (%)	<0.02	<0.3
State of extract	Powder (coal-like)	Pitch-like

To increase the percentage of ash free coal from Indian coal, it is recommended to rigorous study about various parameters like

temperature, pressure and addition of additives. The main motive of this review work is to focus on the various parameters that decrease the mineral matter of coal as well as increase the extraction yield of coal.

Reduction of ash content from coal by agglomeration using binding oil.

It is known that, Froth floatation process for coal beneficiation was extensively used, but this technique works quite well only with high rank coal and fines with larger particle size. This method have some limitation, among them comparatively low yield and high moisture content of product when fines are less than 76 micro meter and have high ash content. Where as, in case of low rank coal, the surface of oxidized coal and mined coal are not able to be beneficiated by floatation process. Hence, this drawback is removed by agglomeration technique.

Since, Agglomeration is a surface phenomenon, 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. Therefore, selection of binding oil to form the aggregates of fine coals must be compatible with the surface functional groups of the fines. Mostly, the binding oils should be Oleophilic in nature and as a result, they get readily adsorbed to the surface of the coal particles provided they have minimal polar groups exposed. The basic assumption of agglomeration technique is the mineral material should be more hydrophilic and oleophobic than the organic coal matrix, the mineral material form a suspension after dissolving in an aqueous medium and thus, the organic matter will form aggregates and separate out from that phase. But, the above technique is true for high rank coals like bituminous coal, not for low rank coals.

In a successful agglomeration process, the inorganic mineral matter of the coal get reduced to a significant value as the coal forms aggregates using binding oil of organic rich material and minerals remained in the aqueous phase. The extent of coal beneficiation by agglomeration is limited by several factors. First one is particle size, if finer particle is used then solid-liquid surface contact is better thus better are the chances to agglomerate of the carbonaceous material with binding oil, and consequently lowering the ash content (Bhattacharyya et al.). It has been reported that the ash reduction in bituminous coal having particle size 320 mesh was more than that of 200 mesh coal showing reductions of 17% and 14%, respectively (Timpe et al.). The second factor which is the composition of the oil used as a binder. Light agglomerating oils (density < 0.90 g/cc) have been shown to give ash reductions in bituminous coals within 10 to 20 percent of those obtained with the Stoddard solvent (Liu et al.). These oils, however, unable to wet the surface of low rank coals in a good way, and are not useful as binding oils for these coals. But, low-rank coals can be agglomerated using heavier oil like petroleum crude, coke oven tars, but once it is used then more difficulty will come in order to recover for reuse (Bhattacharyya et al.).

pH is a third consideration when carrying out agglomeration. Reduction of most mineral material can be done with pH adjustment. However, the presence of pyritic sulfur in mineral matter which can be efficiently removed at a basic condition

(pH=7-11) and the coal becomes more hydrophilic and agglomeration is less effective (Muza et al.).

Apart of this, there are also other factor like higher mixing speeds and longer mixing times has been reported to have removed greater percentage of ash (Sarkar et al.).

### Effect on yield of extraction of different coals

A proper knowledge about the complex structure of coal could help to know its solvent extraction behaviour. Unfortunately this idea about coal structure is still unfinished but a review paper give some light on following points: The structure of coal is like macromolecular having a molar mass distribution ranging between 1300-3500 amu. Apart of this, it contains some amount of relatively low molecular mass substances (between 100-500amu). Probably all known intermolecular forces bind the organic matter of coal together but only presence of hydrogen bonds has been detected directly (Marzec et al.).

Coal can be differentiated by its rank into lignite, sub-bituminous, bituminous and anthracite as well, the rank of coal is define on the basis of characteristic properties like moisture content, volatile matter, ash content and fixed carbon that present in coal. Thus, the result of extraction yield with solvent shows different value (Kim et al.).

For higher rank coals like Bituminous & Anthracite, it has been observed that these coals gives a maximum extraction yield at a peak temperature (called softening temperature) and beyond this temperature the yield decreases (Yoshida et al.). This is related to the thermal relaxation of molecules. Above peak temperature the coal gets restructured and no further release of molecule 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 found 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 give a higher extraction yield as lower MMVR values signify higher reactivity of coal (Rahman et al., 2013).

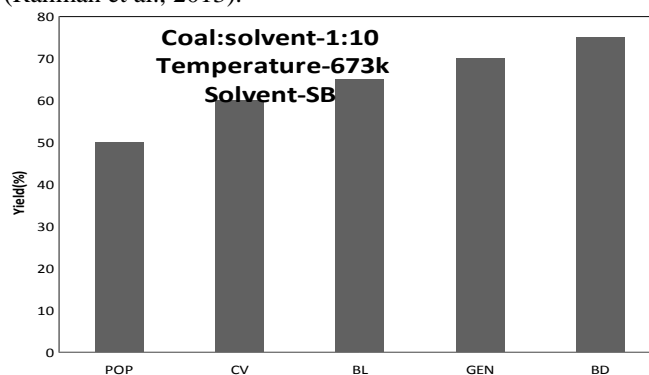


Fig-1: Effect of coal type on extraction yield using hydrotreated heavy aromatic solvent SB with 1 hr of holding time at 673k (Rahman et al.,2013)

### 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 (Miura et al.). The peak temperature at which the extraction yield becomes maximum that has been related to the softening temperature of coal. In bituminous coal, the extraction yield has close correlation with softening temperature showing a correlation index of 0.84 (Yoshida et al.). When the 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 thus releasing mainly small molecules and free radicals from the cross-linking coal structure to the solvent (Okuyama et al., 2004). From the graph, it is clear that that in case of Sunhwa coal, as the temperature reaches to 673k, the extraction yield attains its peak value of 65% and if further temperature increased, it rather goes on decreasing and showing 53% at 703k. This indicates that the extraction can be proceeded more easily near softening point irrespective of solvent's polarity, in case of high rank of coal. In figure 2, Kideko and Roto south are sub-bituminous coals, while Sunhwa is a Bituminous coal (Kim et al., 2007).

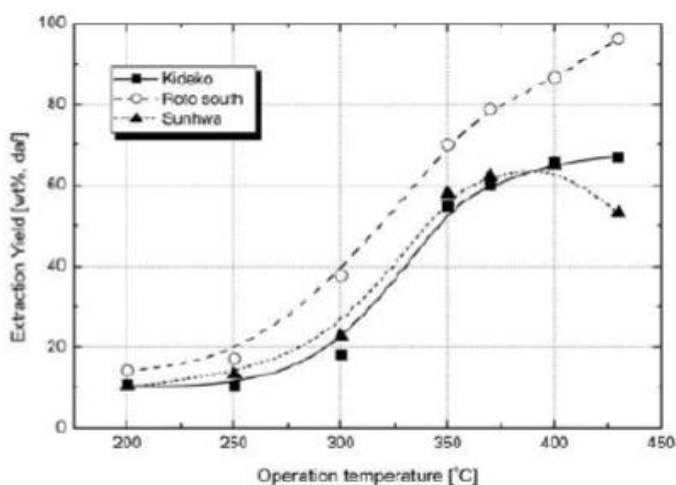


Fig. 2: Variation of extraction yield with temperature (Kim et al., 2007)

For low 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 coal structure (Kim et al., 2007). In above figure, the extraction yield of low rank coal (say Roto south) have not alter very much until the temperature reaches to 527K but rapidly

increased and reached 70% at 623K and even the yield goes on by increasing temperature, showing a higher increase rate than Kideko coal as the yield increased slowly with increase in extraction temperature. 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).

Fig. 3 shows the effect of pressure on the extraction yield of Kideko and Roto South coal. Rise in Pressure of the extractor was little bit different from the change of the initial pressure applied. When the starting pressure was 1 bar, the maximum inside pressure of the vessel raised up to 10-15 bar, and if, at 5 bar and 10 bar, the internal pressure of vessel increased up to 30-50 bar and over 50 bar respectively. Despite the increase of applied pressure initially, however, the extraction yield give the same value as it was i.e below 60% in Kideko coal and around 70% in Roto South coal, showing that there is no significant change in extraction yield. However, when extraction temperature reaches to 673K as the extraction yield at initial applied pressure of 1 bar was around 75% but if the applied pressure increases to 3 bar, the yield increased by up to 90%. These results tell us that the initial applied pressure play no role in order to increase the extraction yield and thus extraction yield can be increased more by raising extraction temperature rather than initial applied pressure).

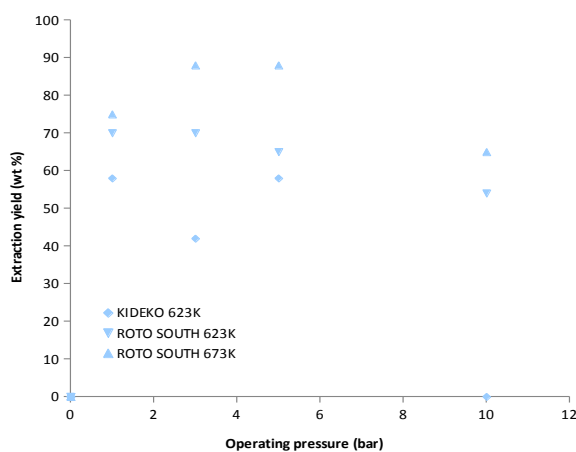


Fig.3: Variation of extraction pressure yield with initial applied pressure (Kim et al.).

### Effect of solvent's nature on extraction of coal

Solvent has property like solvation power which is estimated by all operative solute-solvent interactions. These microscopic intermolecular forces are part of hydrogen bonding, electron-pair-donor and electron-pair-acceptor interaction and also dispersive interactions etc. The polarity of solvent can be measured in empirical way by means of convenient solvent-sensitive reference process (Reichardt et al.). when coal is dissolved in solvent, coals starts swelling. The extent of coal swelling appears to correlate well with the solvent electron-donor number (Marzec et al.). But swelling mechanism of macromolecular structure of coal in basic solvents is one of breakage of hydrogen bonds, even he founds that swelling

properties is related to Pkb value rather than electron donor number values. (Hall et al.).

For higher rank coals, it has been reported that mixture of bituminous coal and non-polar aprotic solvents like 1-methylnaphthalene (1-MN), Toluene, DCM can give satisfactory yields of about 70% by weight (daf) and ash content reduced to several hundreds of ppm at 613- 632K ( Okuyama et al., 2004, Yoshida et al.). However, if a non-polar protic solvent like tetralin is used, the extraction rate becomes more than that obtained as in former case at same condition. This is due to intermolecular hydrogen transfer from the solvent to the coal so that small thermally decomposed molecules from coal gets stable and coal softening phenomenon brings about this process ( Okuyama et al., 2004.). Polar solvents like NMP ( N-methyl-2-pyrrolidione, C<sub>5</sub>H<sub>9</sub>NO) was used as a solvent. NMP is a 5-member ring, which has a boiling point of 475k and is water soluble. This NMP have been reported to have given extraction yields of above 60% for Bituminous coals at temperatures above 643K (Kim et al., 2007). Japanese bituminous coal is also extracted by the use of pyridine and quinoline in an autoclave under 1Mpa of nitrogen pressure at 473-673K separately. After extraction process, extraction yield using pyridine results into 50 (wt%) at 673K, whereas yield using quinoline gives 80% at 623K. Thus, it clearly states that polar aprotic solvent show higher extraction yield irrespective of coal types.

However, for low rank of coals, such as lignite and sub-bituminous coals, there is no softening temperature 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 that a polar aprotic solvent like NMP can give an extraction yield of over 80% at a temperature of about 400°C (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 considered a powerful solvent than non-polar ones for the low rank coals which have much of polar sites ( Li et al., 2000).

Apart of this, there are many different type of solvent which are used for extraction purpose. Some of them are CMNO, CQ, LCO (an industrial solvent), MW-S (methanol-water soluble), MW-I (metanol-water insoluble), AC-S and AC-I. From the bar graph, it is clear that Using above mentioned solvent, the extraction yield of Wyodak Anderson sub-bituminous coal gives 73% with MW-S which is much higher (around 32%) than with CMNO. Solvent AC-S also give a high yield approx 63% also the yield using AC-I is similar to that with CMNO, whereas extraction yield with MW-I is lower than CMNO (Kashimura et al.).

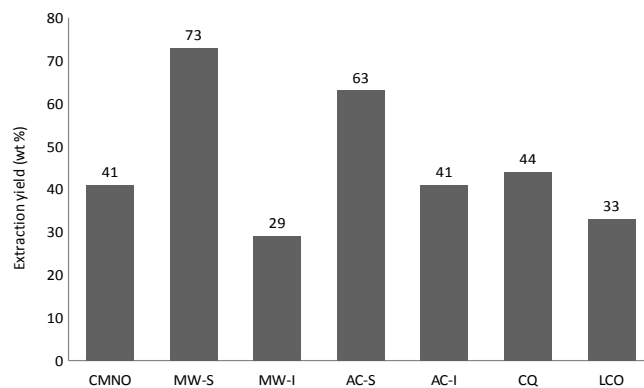


Fig-4: Extraction yields with industrial solvents and CMNO-derived

### Effect of hot and cold filtration on extraction yield

It has been observed that the high extraction yield of coal can be achieved 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 ( i.e Ash free coal) (Okuyama et al., 2004). This happens because the extract components soluble at high temperature might have deposited while quenching and thus decreased the percentage of extraction yield (Yoshida et al., 2001).Hence, filtration after extraction should be performed at high temperature to maintain a satisfactory extraction yield.

### Beneficiation by mixture of solvents

Beneficiation of coal using mixtures of solvent, like CS<sub>2</sub>-NMP (in the ratio 1:1 by volume) has been reported to have given a higher extraction yield (40-65 wt.% for many bituminous coal) than using pure NMP. Basically, Two factor which have great contribution towards the extraction of coal, one is the solubility of solvent to coal and other one is penetration ability of solvent into cross-link structure. NMP, it is a polar aprotic solvent (i.e polar solvent but can' donate hydrogen atom) and known as better solvent for bituminous coal extraction because the N-methyl-2-pyrrolidinone ring (A five member ring) interact greatly with aromatic rings, especially for polycondensed aromatic compounds. However, yield of coal using NMP solvent alone gives low value cause of its high viscosity and low penetrability, thus it enters only the upper free-por coal but unable to enter the cross-link structure of coal. But when CS<sub>2</sub> is added to NMP then it produce an effect greater than the sum of their individual effects called synergistic effect. It has been found that with the CS<sub>2</sub> addition, Solvent mixture's viscosity decreases from 1.69 mPa s to 0.615 mpa s and penetration power of solvent mixture to the cross-link coal structure increases, so that solvent soluble molecules interact with that mixed solvent to large extent, thus the extraction yield increases (Shui et al., 2004). CS<sub>2</sub> is reported to have large synergistic effect with many of different solvent for extraction of bituminous coal at room temperature. For example,



Tetramethyl- urea and pyridine are effective too when used as mixed solvent with CS<sub>2</sub> (Takanohashi et al.).

For low rank of coal, The mixed solvent CS<sub>2</sub>/NMP is ineffective for extraction. For Loy yang coal, its extraction yield decreases from 14.3% of Nmp to 10.9% (daf) of the mixed CS<sub>2</sub>/NMP solvent. This may happen due to the difference in active interacting site with solvent between low rank coal and bituminous coal. NMP/HHA (1,4,5,8,9,10 Hexahydroanthracene) mixed solvents have been reported to produce a large synergistic effect when it is mixed with coal and the dissolution yields increases, 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 radicals is the key reaction (Li et al., 2000). It has been found that extraction yield using a ternary solvent system CS<sub>2</sub>/NMP/Tetracyanomethylene was 84.6 (wt%) (Ishizuka et al.).

Some of model solvent can be prepared by mixing of polar material like QN,IN,IQ or MQ(these are derived from the fractionation of CMNO solvent.) with MN (methylnaphthalene).

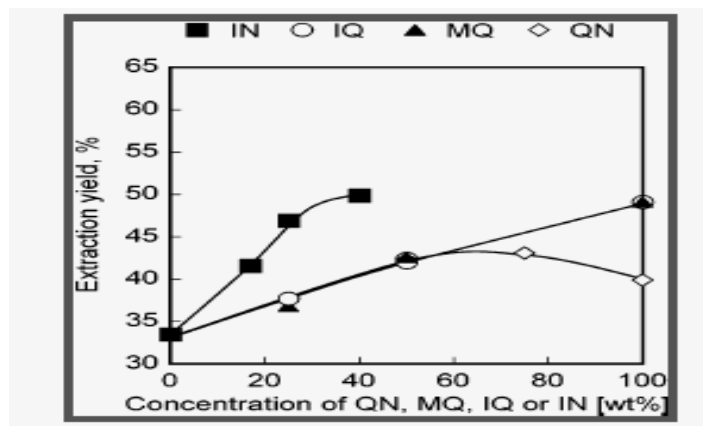


Fig-5: Extraction yields with the mixture of QN, MQ, IQ, OR IN with MN

Figure represents yield of wyodak coal when mixed solvent of MN and each polar materials for varying their concentration is used. From the above figure, it is clear that the extraction yield in absence of polar materials is 34% and increases from 34% to 42-43% after adding polar material about 50-75 wt% QN. Even adding of MQ/IQ to MN also increases the extraction yield. The extraction yield reaches to 50% by adding 40% of IN concentration. These information states that IN is more powerful at coal dissolving than QN, IQ OR MN. The main reason behind this is the presence of pyrrole-type nitrogen(i.e it can donate hydrogen) in IN whereas other polar material have pyridine-type nitrogen. But, it does not sounds like presence of IN component is the key factor in order to get high extraction yield, As it has been observed that A mixture of IN and MN gave 50% yield when 40% of IN concentration is added, while MW-S shows a yield of 73%, even it contains only 25% IN. Thus extraction yield of MW-S is not explained by the effect of IN alone. In other words, we can say that extraction yield does

not rely on the major components, such as QN, IN, IQ and MQ, but also on other minor components like methanol (Takanohashi et al.).

### Effect of various additives

It has been observed that the degree of dissolution of coal in solvents like NMP, DMF, can be enhance using additives like strong bases ( NaOH, Sodium tertiary butoxide etc.). Depending on the extraction conditions, carbon extraction efficiencies of up to 90% have been obtained, (Makgato et al., 2008) as shown in figure given below.

Sodium, or, potassium hydroxide is added as a solution with water. However, it has been reported that the water can be detrimental factor for DMF ( Actually, the presence of water tend to base catalysed hydrolysis of DMF which produce dimethyl amine and formic acid). If sodium sulfide is further added then it can reduced the ash content of the extracted coal. It has also been found that if molar ratio of NaOH/Na<sub>2</sub>S became high, the extraction of coal gets increases ( Makgato et al., 2008).

By adding small amount of polar material (say methanol) to nitrogen-containing polar solvent, it shows a great increase in the thermally extracted yield for sub bituminous coals (Takanohashi et al., 2006). Adding salts such as lithium and tetrabutyl-ammonium salt with different negative ions to either polar aprotic solvents or to solvent mixtures have shown increase in the extraction yield for several coals. The extraction yields goes on increasing in the order of F->Cl->Br->I-, which indicates that element having high electronegativity are responsible for enhancing the yields. Since, the solvent is polar as well as aprotic ( i.e no hydrogen donation), thus the high electronegative element such as F- & Cl- do not get solvated due to absence of proton as they needed it. Hence the bases will interact only with acidic sites in the coal ( Takahashi, 2001). But the bases with low magnitude of electronegativity like Br- & I- show opposite result i.e they dissolved in soft acid like CS<sub>2</sub>/NMP mixture and hence they do not interact with acidic site of coal. ( Takahashi, 2001). Similarly, It has been observed that the adding LiCl (alkali metal salt) enhances the polarity of the solvents-salt solutions and increases the coal extraction. It has been reported that industrial solvent like CMNO (crude methyl naphthalene oil) contain some polar material and these polar materials can be separated by fractionation process. Using extracted polar material, The yields are 20-30% more than that with CMNO ( Kashimura et al., 2006). It has been reported that CMNO has major component ( Quinoline) and the minor constituents are isoquinoline, indole and methylquinoline. Since the result states that indole is more capable in order to extract coal constituents than quinoline. But when mixture of indole and quinoline is used with a non-polar solvent, then a higher extraction yield compared to quinoline-nonpolar solvent mixture is obtained ( Kashimura et al., 2006).

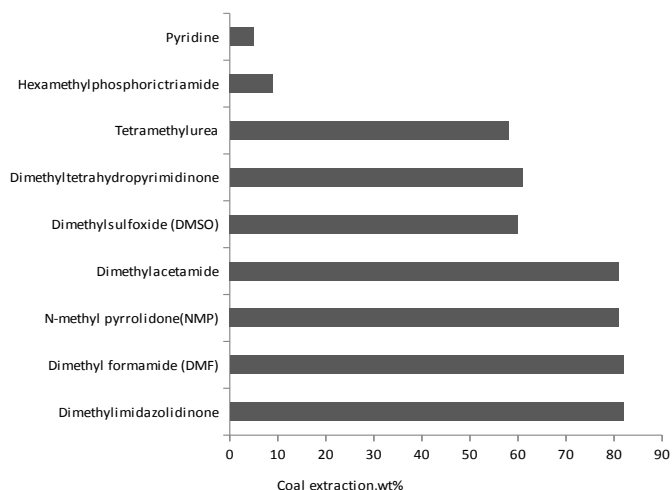


Fig-6: The effect of solvent nature on the extraction efficiency at ambient conditions. Solvent:coal:KOH=100:10:1.56 on a mass basis (Makgato et al.).

#### Effect of extraction time on yield of coal

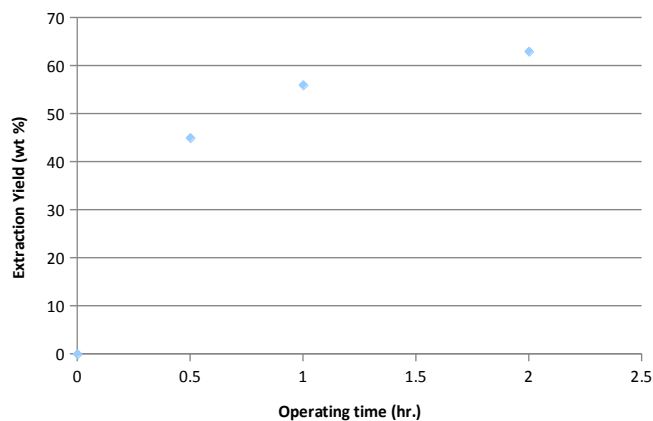


Fig-7: Variation of extraction yield with extraction time for the Kideko coal (623K, 1bar) (Kim et al.).

Above figure shows the variation of extraction yield associated with time in Kideko coal. If the temperature is kept constant throughout the extraction process (say at 623K), the coal extraction yield increases from 50%-60% when the extraction time is extended to 0.5hr and 1hr respectively (Lee et al.). Similarly, for case of lignite coal, the extraction yield remain same either for 1hr or 2hr extraction process but it increases when the extraction time is set for 3hr compare to 1hr or 2hr.

#### Conclusion

Ash content from coal can be successfully reduced to appreciable amount using proper solvents. Both polar and non-polar solvents can be used for the extraction of high rank Bituminous coals, But in case of low rank coal, only polar

solvent can rupture the coal structure for greater dissolution of coal. The extraction yield depends on many parameters, like nature of solvents, types of coal used, the extraction temperature as well as time of extraction. The extraction temperature is again related to the softening temperature in case of Bituminous coals, But not in case of low rank coals so extraction yield increases with increasing temperature. After completion of extraction process, The residue and filtrate part of coal in a vacuum filtration unit should be performed near the extraction temperature so that a high extraction yield is obtain, otherwise carbonaceous part of coal which soluble at a high temperature may precipitate out while quenching at lower temperature. The presence of certain additives, like polar compounds containing nitrogen can increase the extraction yield from the coal. Thereby decreasing the ash content of the extracted coal.

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