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Effect of nanoparticles on the structural changes of char prepared by non-isothermal treatment of Assam coal (India) in nitrogen atmosphere

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Abstract
Structural changes of char prepared by thermal treatment of Assam coal in absence and presence of mixed metal oxide nanoparticles (cobalt ferrite) have been studied here. Thermogravimetric (TG) analyses were carried out in nitrogen atmosphere up to 250°C at a heating rate of 5°C per minute. TG studies for the raw coal sample shows no weight change in the temperature range 110-245°C suggesting phase transition with the formation of a softening state while there appeared minor weight gain in this temperature range for the mixed metal oxide nanoparticles blended coal sample. The effect of nanoparticles in the thermal treatment of coal is apparent and thus restricting the devolatilization to certain extent, due to the increase of thermally stable components. The chars prepared from these samples at 250°C in inert atmosphere, have been used to compare the changes of structure in the absence and presence of nanoparticles by using FTIR studies. Modification of structure of the raw coal char by the formation of oxygen containing species and increase of aromaticity in the char of the blended coal sample has been reported here. It appears that the presence of mixed metal oxide nanoparticles has been playing a dominant role in the structural changes of coal during thermal treatment in inert atmosphere. This work has some considerable technological interest.

Keywords: Coal, Blended coal, Nanoparticle, Char

1. Introduction
Coal is one of the major conventional energy sources on the earth. Owing to the increasing energy demand, the risk of petroleum shortage and too high prices, most countries of the world are interested for utilization of coal. Large increase of coal utilization in various industrial purposes calls for understanding its physical properties and the chemical environments. Worldwide applications of coal for the generation of electricity, production of industrial cokes as well as works on gasification, liquefaction, etc., besides usual firing purposes in industrial establishments throughout the globe play a major role from the view point of fuel security and cost.

Coal is a polymeric substance and has an open macromolecular amorphous structure [1] having large surface area with varying sizes of pore [2]. It contains aromatic and aliphatic compounds with varying molecular weights; the thermal behaviours of these compounds are not alike. As the percentage of carbon in coal increases, the aromatic content increases, oxygen content decreases and calorific value increases [2]. Due to heterogeneous nature of coal, certain molecules are remaining undisturbed and the rest could undergo some modification in the thermal treatment of coal [3]. Those molecules which are less thermally stable, could undergo decomposition, transformation, and release as volatile species, bond cleavage and even phase change. However, these mainly depend on the rate of heating, atmosphere of heating and the extent of temperature. Fuel value of coal material increases as there is increase of thermally stable species occurring in the coal product. The evolution behaviour of volatile species is very important for knowing the types of chemical changes occurring during devolatilization and not for weight loss characteristics. If devolatilization can be restricted, less weight loss during thermal treatment can be achieved. Evaluation of thermodynamic parameters in air and nitrogen atmospheres for phase transition of Assam coal has been reported [4]. The pyrolysis of coal in presence of inorganic compounds such as $AlCl_3$, $SbCl_3$, $ZnCl_2$, $SnCl_2$ [5-7] and mineral pyrite [8] have been reported to show the modification of the coal molecule through different mechanisms. Decomposition, devolatilization, formation of new compounds, etc., on pyrolysis in presence of inorganic species, emphasise the importance of applied coal research.

The purpose of this study is to investigate the thermal behaviour of coal molecules in low temperature. Under the present investigation, it is planned to study how does devolatilization (or weight loss) could be restricted to some extent using a nanoparticle catalyst. An attempt will also be made to understand the chemical environment of coal char due to restriction of devolatilization.

2. Materials and methods

The coal sample for this study was collected from Tirap colliery of the Makum Coal Field, Upper Assam, India. The coal was treated with 4M HCl followed by 2M HNO_3 and then washed with double distilled water and finally dried in air. The coal sample was kept in an air tight polypropylene bottle. This sample is termed here as raw coal sample.

The proximate and ultimate analyses of the coal sample are given in Table 1.

Table 1: proximate and ultimate analysis of coal sample

Proximate*		Ultimate**	
Moisture	4.9 Wt. %	Carbon	79.3 Wt. %
Ash	28.5 Wt. %	Hydrogen	5.5 Wt. %
Volatile matter	33.8 Wt. %	Nitrogen	1.3 Wt. %
Fixed carbon	32.8 Wt. %	Sulphur (organic)	3.7 Wt. %
		Oxygen (by difference)	10.2 Wt. %

*As received basis **Moisture free basis

Cobalt ferrite nanoparticle was used for this study as a catalyst. The preparation and characterization of the nanoparticles (200 nm) was reported elsewhere [9]. The amount of 0.5 mg of the nanoparticle was thoroughly mixed with 100 mg of the acid washed coal and kept in an air tight polypropylene bottle. This sample is termed here as blended coal sample.

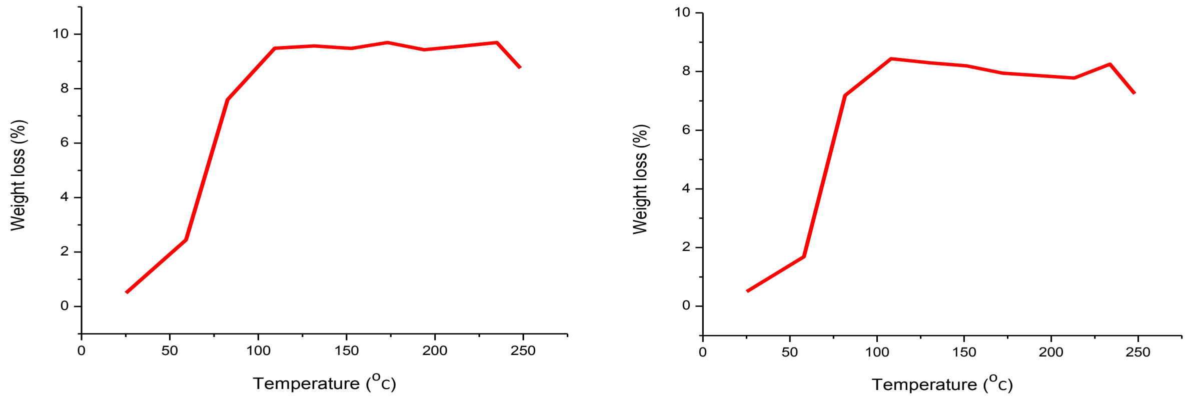
The raw coal and blended coal samples were separately heated non-isothermally in nitrogen atmosphere. For this purpose, thermogravimetric analyses were carried out in DTA-TGA instrument (Model SDT 2960) of M/s TA Instrument, USA. The rate of heating was maintained at 5°C per minute in the extent of temperature up to 250°C.

FTIR spectrum of each of the samples was recorded in a FTIR 2000 system (Perkin-Elmer) in the range 400-4000 cm^{-1}. For the pellet, coal to KBr in the ratio of 1:200 was taken and the pellet was finally prepared by applying 20 tons pressure.

3. Results and discussion

3.1 Thermogravimetric studies

The TG curves for the raw coal and the nanoparticle blended coal samples are given in Figure 1. In the TG curve, initially both the samples show minor weight loss. Initial weight loss up to temperature 110°C is due the loss of moisture associated with the samples. The weight loss for the raw coal up to 110°C is slightly higher than that of the blended sample. Beyond the moisture removal temperature, no significant weight change has been found in the samples. In the raw coal, the weight loss between 110-275°C is marginal. Almost constant weight loss for this temperature range in this sample strongly reveals phase transition of the coal molecule.



(a) (b)

Figure 1: TG curve for (a) raw coal (b) nanoparticle blended coal

Softening of coal takes place by molecular disruption. Fluidity is associated with decomposition giving rise to smaller molecules, which have sufficient mobility to produce the overall plasticity [10]. Since coal is a mixture of heterogeneous molecules, therefore, it is not appropriate to mention that all the molecules might undergo phase transition. A certain number of molecules underwent phase transition from solid to a softening state. Due to phase transition of some molecules and thermal stability of the other molecules in the raw coal sample, no loss of weight has been found in the TG curve. A distinct difference of the TG curve is observed in the nanoparticle blended sample. Firstly, in this sample, relatively lower value of the weight loss up to temperature 110°C has been observed which is mentioned above. Beyond 110°C, the weight loss decreases up to 245°C and then increases again. However, the weight gain in the temperature range 110-245°C is not significant but distinct in the TG curve. Like raw coal sample, certain molecules in the blended coal samples could also undergo phase transition; the formation of new compounds in the presence of nanoparticles cannot be ruled out. Therefore, the influence of nanoparticles on the coal molecules during non-thermal treatment in nitrogen atmosphere needs discussion.

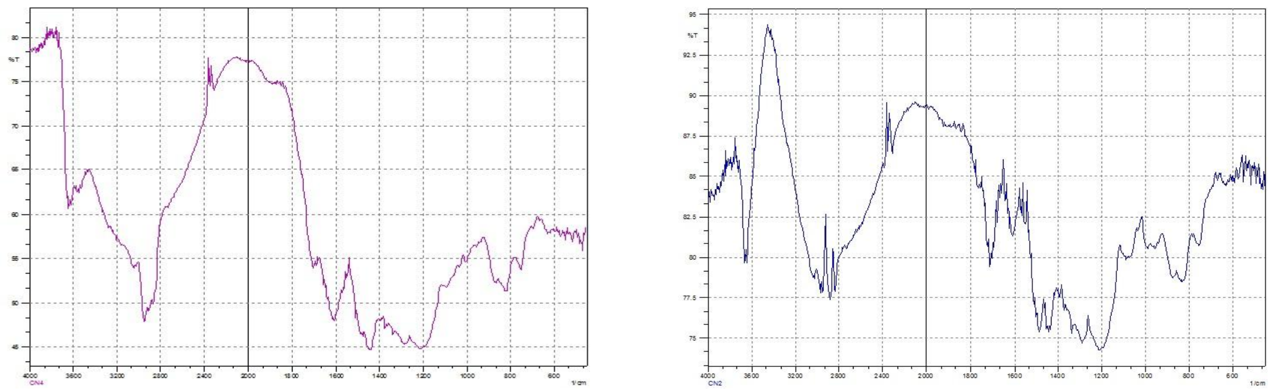
The mixed metal oxide nanoparticles, cobalt ferrite, could act as a catalyst in the modification of coal molecules through different mechanisms during low temperature thermal treatment at a heating rate of 5°C per minute. Three simultaneous processes may be possible during heat treatment in nitrogen atmosphere: (a) some molecules could undergo phase transition, (b) some thermally unstable molecules could decompose in presence of nanoparicles and formed free radicals, and (c) free radicals might combine themselves to form bigger molecules and might combine with some species produced in the system.

During thermal treatment, both raw coal and blended coal samples should show similar pattern of the TG curves. Dissimilar nature of the TG curves reveals contribution of nanoparticles in the thermal behaviour of the coal molecules. If no external species are occurring in the thermal process, weight gain in the blended samples is not possible; however, mechanism of the modification of the molecules may be different. Since weight gain is observed in the blended sample in the temperature range 110-245°C, this strongly suggest that some species might have been produced during non-isothermal treatment in presence of the catalyst. These species further react with coal molecules or free radicals resulting in increase of weight.

Moisture content in both raw coal and blended coal samples should be same because the blended sample contained nanoparticles of only 0.5%. But surprisingly, the removal of moisture up to 110°C is different in these samples. Removal of lower moisture content in the blended sample suggests that during thermal treatment in nitrogen, the nanoparticles could interact with some moisture content and could form hydrogen and oxygen species. These species might combine with the decomposed product of coal yielding new molecules and as a result weight gain has been noticed in the TG curve for the blended sample in the temperature range 110-245°C. The increase of weight loss beyond 245°C may be correlated with the release of low molecular weight volatile species. Lower weight loss in the blended sample gives an important result that the char obtained by the thermal treatment of this sample contains a higher percentage of thermally stable molecules than the char obtained from the raw coal. This strongly reveals about the restriction of devolatilization (or weight loss) of coal to some extent during thermal treatment. Thus it is evident that during thermal treatment in inert atmosphere, the presence of nanoparticles has a profound influence on the structural changes of coal by increasing the thermal stable molecules in the char. The chemical environment of the molecules contained in the char can be studied with help of infrared spectroscopy.

3.2 FTIR studies

FTIR spectra of the chars obtained from the raw coal and the blended coal samples are given in Figure 2. The C-H stretching vibration occurs broadly in the region 2800-3000cm^{-1}[11]. The bands at 2926 and 2853 cm^{-1} are due to asymmetric and symmetric stretching vibration of the C-H of methylene groups, respectively. The band at 3050 cm^{-1} may be assigned to C-H stretch of aromatic units. In the char of the raw coal, one weak band at 3090 cm^{-1} and a sharp band at 3020 cm^{-1} have occurred. This reveals that the raw coal has considerable aliphatic components. This is possible because the coal sample, under study, is a low rank coal and, therefore, the predominance of aliphatic components is justified. On the other hand, the spectrum of the blended coal sample (Figure 2) shows a number of bands in the range 2800-3000cm^{-1}. Although two bands in this region appeared but an additional band at 3050 cm^{-1}. The band at 3050 cm^{-1} for the char of the blended coal sample may be assigned to aromatic units; however, this band is not distinctly found in the char of the raw coal. This provides an important result of the newly formation of the aromatic components during thermal treatment in presence of mixed metal oxide nanoparticles.



(a) **(b)**

Figure 2: IR spectra of char (a) raw coal and (b) nanoparticle blended coal

Painter et *al.* [12] reported that aromatic ring stretching and deformation modes can be observed in the region 1450-1550cm^{-1}. A greater absorption in this region is an indication of greater aromaticity. One distinct band in the char of the raw coal and two distinct bands for the char of the blended coal samples are observed in this region. Greater absorption of the bands found in the char of the blended coal sample suggests greater aromaticity. Therefore, the effect of mixed metal oxide nanoparticles in the thermal treatment of coal is noteworthy. An absorption band for hydroxyl group is generally found above 3600cm^{-1}. The absorption of the band at 3625cm^{-1} in the char of the raw coal is quite low. In the char of the blended coal, the spectrum shows high absorption of the band; precisely two distinct very adjacent bands appeared. This strongly suggests occurrence of some structural changes which are accompanied by the increase of the hydroxyl groups due to the presence of nanoparticles. There is a strong likelihood that this could be due to the interaction of minor moisture content with the nanoparticles. Higher quantity of the hydroxyl groups in the char of the blended sample could be due to the presence of more cross linking. Further appearances of three distinct bands in the range 900-1000cm^{-1} in the char of the blended sample are assigned to out-of-plane bending vibration of O-H bonds. These results distinctly prove that there occur some structural changes of the coal molecule during thermal treatment in the presence of metal nanoparticles. Both the chars give a distinct band around 1600cm^{-1}which is assigned to asymmetric and symmetric C-C stretching vibration. An important observation noticed is that same medium intensity of the band for the two chars supports that no vigorous cleavage of the C-C bond took place in the non-isothermal treatment in nitrogen atmosphere. This result is quite contrary to our observation of the no or very minor weight change in the thermal process (Figure 1). Although ether linkages are common in coal molecule, but no distinct band at 1020cm^{-1} in the two chars has been observed. According to Silverstein *et al.* [11], vibrations involving oxygen atom result in greater dipole moment changes and thus, more intense bands are observed for the ethers. In the spectrum of the char of the blended coal sample, a sharp band with high absorption appeared at 1730cm^{-1} for C=O stretching (Figure 2), but this band is found to be weak in the spectrum of the char of the raw coal sample. This is also an important observation of the structural change of the coal molecule during thermal treatment in presence of nanoparticles. It is now evident from the present study that the variation of weight change as found in the thermogravimetric studies for both raw coal and blended coal samples is highly supported by FTIR studies. The decrease of weight loss in the blended sample during thermal treatment indicated formation of thermal stable molecules which are confirmed by the formation of oxygen containing species and increase of aromaticity.

Conclusion

The non-isothermal treatment of unblended and cobalt ferrite blended (magnetic nanoparticle) Assam coal at low temperature (up to 250°C) under nitrogen atmosphere give some interesting results. Due to the effect of nanoparticle during pyrolysis of coal, decrease of volatile matter was observed. The different patterns observed in the temperature region 110-245°C in the samples in presence and absence of nanoparticles has been observed. Weight gain in blended sample could be due to the formation of some bigger molecular species as well as by the formation of oxygen containing species and increase of aromaticity in the char as evident from the FT-IR studies.

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References

1. Nava R., Amorer L., Percina S., *Fuel* 73 (1994) 51.
2. Van Krevelen, D.W., *Coal: Typology-Chemistry_Physics-Constitution*, Elsevier, Armsterdam, 1981.
3. Ceylan K., Kareca H., Oval Y., *Fuel* 78 (1999) 1109.
4. Borah J.K., Barua M., Borah D., Baruah M.K. *Proceedings of 6th Asian Thermophysical Properties Conference*, M.N. Bora (Editor), 1 (2001) 87.
5. Butler R., Snelson A., *Fuel* 59 (1980) 93.
6. Buchanan III A.C., Dworkin A.S., Smith G.P., Buchanan M.V., Olerich bG., *Fuel* 60 (1981) 694.
7. Weller S. Pelipetz M., Friedman S., Storch H.H., *Ind. Eng. Chem* 42 (1950) 330.
8. Borah D., Barua M., Baruah M.K., *Fuel Process. Technol*. 86 (2005) 977.
9. Senapati K.K., Borgohain C., Phukan, P., *J. Mol. Cat. A: Chemical* 24 (2011) 339.
10. Das T.K. *Fuel* 80 (2001) 489.
11. Silvetrstain R.M., Bassler G.C., Marrill T.C., *Spectroscopic identification of organic compounds*, John Wiley & Sons, New York, 1981.
12. Painter P.C., Kuehn D.W., Starsinic, M., Davis A., Havens, J.R., Koenig, J.L., *Fuel* 62 (1983) 103.