Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc
Petroleum & Coal 53 (1) 45-55, 2011

COMPOSITION AND STRUCTURE OF LUXING COAL WITH DIFFERENT PARTICLE SIZES

Yueqin QIU[1], Qin ZHANG[1], Yingzhong TIAN[1], Jie ZHANG[1], Jianxin CAO[1], Tiancun XIAO [1, 2*]

[1]Guizhou University-CSCSTUK Clean Energy Centre, School of Mines, Guizhou University, Caijiaguan Campus, Guiyang City, 550003, Guizhou, China
[2]Inorganic Chemistry Laboratory, Oxford University, South Parks Road, OX1 3QR,
email: xiao.tiancun@chem.ox.ac.uk

Received October 22, 2010, Accepted February 1, 2011

Abstract

More than 10 tons of coal samples from Luxing Coal Mining Company, Guizhou Province have been collected from various points and sieved into different sizes from the as mined products according to its market demand and utilization. The series samples with different sizes have been characterized using X-Ray diffraction (XRD), Laser Raman (LR), Infrared spectroscope(IR), ^{13}C solid state magic angle spinning nuclear magnetic resonance (^{13}C MAS NMR), and scanning electron microscope. It is seen that the bigger lump coal has higher pyrite content and quartz, the big lump coal normally has higher inorganic sulphur content, while the coal powder has higher organic sulphur content. In addition, the coal powders with smaller size have higher dolomite content. The kaolinite and quartz are present in the coal with various particles size. The carbon in the Luxing Coal is present in good crystalline structure, in which 95% of the coal is graphitic structural in the coal with smaller size.

Key words: Puan coal; structure; composition; different particle size.

---

1. Introduction

Coal has been one of the main energy sources for hundred years, and will likely continue to be one in the future [1-3]. It is a widely differing natural rock that consists primarily of organic materials admixed with smaller quantities of mineral matter including sulphur [4]. The organic materials in coal are mainly composed of large polymeric molecules derived from complex plant materials by complicated chemical and biological reaction processes. The structure and composition of coal depend mainly on the formation process and the geological conditions during and after the organic transformation. The mineral matter may occur both as mineral species and mineral phases of extremely various particle sizes and as species that are chemically complexed by the organic matter. The structure and composition of the coal decide the way the coal is utilised [5].

The physical structure of coal is taken to represent the spatial arrangement of the large complex molecules, along with a few much smaller ones. The physical structure of coal may be studied with profit without going to the detailed knowledge of the chemical structure of the large coal molecules [6-8].The chemical structures of the organic molecule in coal vary greatly, particularly with its rank. Indeed, it appears that the chemical structure of coal and even coals of substantially the same region show more differences than similarities. On the other hand, the physical structure of coal appears to show more similarities than differences.

In China, coal is the primary energy source which accounts for 75% of the national energy consumption. Guizhou province is the main producer of coal in South China, with an output of up to 0.12 GT in 2006. The proven coal minable reserves are up to 49.8 billion tons in Guizhou Province. Because of the high content of mineral matter, sulfur, and trace metallic elements in coal, many researchers have studied the concentration and occurrence of hazardous trace elements in coal from this area [9-11].

Puan Coalfield is located in the western Guizhou (Fig. 1) and consists of Late Permian [12] coal-bearing strata. Permian coal-bearing strata in the Puan Coalfield include the Upper Permian Emeishan Formation (P1e), the Late Permian Longtan Formation (P2l), the Late Permian Changxin Formation (P2ch), and the Late Permian Dalong Formation (P2d). The

---

*corresponding author: xiao.tiancun@chem.ox.ac.uk

Longtan Formation (P2l) is the main coal-bearing formation in the study area and consists of sandstone, siltstone, mudstone, limestone, and coal, with a total thickness about 250–320 m [12]. Its sedimentary environment varied from lagoon and tidal flat through lower delta plain to tidal flat and carbonate subtidal flat.

There have been studies on desulphurisation, demineralisation and trace metal content analysis in Puan coal based on the assumption that it is used as the fuel. So far, there have been little reports on the structural parameters. It is well-known that the role of X-ray study in carbonaceous materials is important. X-ray scattering from coal may provide insights into the relative arrangement of carbon atoms in its matrix. Fourier transform infrared (FT-IR) spectroscopy is also a powerful tool for characterisation of coal and its products as it rapidly builds a comprehensive view of the structure/composition of the materials. In the present work, both FT-IR and XRD have been used to study the structural aspects of Luxing coal samples from Puan County, Guizhou Province.

On the other hand, there have been lots of studies on the coal treatment and conversion, especially on the desulfurization due to the increasing environmental regulations. So far, most work has been based on the analyses of the overall sample, which are all based on the uniform evenly sampling [13-21]. In fact, when coal is mined, the mined products are normally sieved into different size and supplied according to the utilisation. For example, the lump coal is normally sold at higher price to the coking industry or steel industry, while the smaller coal powder is sold for power generation. It is expected that the coal with different composition and structure would be present in different shapes during the mining, because of the strength and binding capability of the different compounds such as quartz, carbon, kaolinite and pyrite which are normally present in coal.

In this paper, large amounts of samples were collected from a coal field from Puan, and the samples have been classified according to the particle size. The samples with different particle sizes have been characterised using XRD, ^{13}C NMR, elemental analysis, FTIR, and laser Raman. Some interesting results are obtained.

2. Experiments

2.1. Sample collection and preparation

Freshly mined coal samples were collected from Luxing Coal Mining Field, Puan County, Guizhou Province. Puan County is located at latitude of 25°18 to 26° 10′35″N and longitude of 104°51′10″ to 105°09′24″E. The detailed location of Puan county, Guizhou Province is shown in Fig. 1.

More than 100 Kg of samples was randomly collected from different points of mined coal batches. Generally speaking, the mined coal from Luxing does not have big lump size. Most of the coal is less than 50mm. The as-received sample is sieved into different sizes, e.g., the part with >25mm, 13-25mm, 6-13mm, 3-6mm, 0.5-3mm and 0-0.5mm. The amount of each part is weighed to determine its proportion in the total sample. The moisture content, ash, sulphur content and volatile component in each part are analysed according to the Chinese standard GB 5751-1986.

2.2. Physico-chemical analysis of coal samples

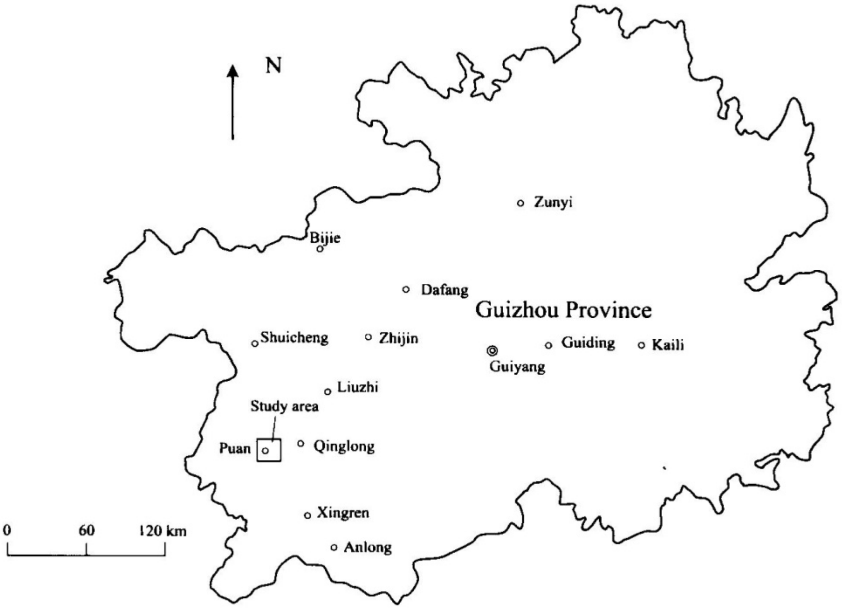
The proximate analyses of the coal samples were done by standard methods (IS: 1350 (Part I) 1984). The elements C, H, N and S were analysed by an elemental analyser, The PerkinElmer 2400 Series II CHNS Elemental Analyzer. The calorific values were determined using Bomb calorimeter (ASTM D 3286). The analyses of the coal samples are given in table 1. The ash analysis of the coal samples was carried out by standard methods (Vogel 1969; Karr 1978b). All analyses for the samples were carried out in quadruplicate and mean values have been reported.

Table 1

	M_{ad}/%	A_d/%	$S_{t,d}$/%	Vd	Qbad (kJ/g)
Overall coal sample	2.33	18.47	3.4	9.8%	30.43

The crystalline structure of the samples were determined by X-ray diffraction using a Philips X′ PeRT Pro Alpha 1 diffractometer with Cu Kα radiation (λ= 1.5406Å) operated at a tube current of 40 kV and a voltage of 40Ma. Data were collected over 2θ values from

20^0 to 80^0, at a scan speed of 1^0/min. Laser Raman spectra were obtained using a Perkin Elmer 400F Ramanstation Raman spectrometer. Fourier transform infra red (FTIR) spectra were carried out by diffused reflectance using a Bruker Vertex-70.



The morphology of the coal samples was observed with scanning electron microscopy (SEM) on a Hitachi S-520 microscope operated at 20 kV and 40 mA. Raman spectra were recorded with a resolution of 2 cm^{-1} using an Yvon Jobin Labram spectrometer with an Ar+ laser (514.5 nm) running on a back-scattered confocal arrangement. The samples were pressed on a microscope slide and the scanning time was set to 60 s. The scanning range was 90 to 2500 cm^{-1}.

Solid-state MAS NMR measurements were carried out in a CMX-200 NMR spectrometer at a frequency of 50.31 MHz. The strongly metallic samples were diluted to 40% with sodium chloride and ground finely before packing into the 7 mm zirconia rotor, fitted with boron nitride inserts. Typically 20 000 transients were collected using a single pulse (45°), with a pulse delay of 1.0 s and a 4 kHz spinning speed. The spectra were recorded at room temperature using adamantane (δ = 29.5) as the reference.

3. Results and discussion

Normally in Guizhou, when coal is mined and sold as fuel for combustion, it is required to measure sulfur content, ash, moisture and volatile matters. The index of the coal as fuel is shown in Table 1. The overall sample has sulfur content of 3.4%, suggesting it is the coal fraction with the highest sulphur content. Its moisture content is 2.33 wt% and ash content 18.47% after combustion. The heating value is 30kJ per gram, volatile content about 9.8%.

When the coal is classified into different sizes, weighed and analysed, the results are shown in Table 2. It is interesting to see that the amount of coal with size bigger than 25mm is 22% of the total coal sample, coal with particle sizes of 13-25mm is about 13%, while the coal content with 6-13 mm of size account for 23.9% of the total coal amount, which is the dominant amount in the sample. Interestingly, the fine powder accounts for 8.97% of the coal sample, the 3-6mm sized coal is the second least, and 3-0 mm sized coal has 18.5 of the total coal samples. In terms of Mad, 13-25mm samples has the lowest moisture content, only 0.95%, while the one with bigger size >25mm and small size 0.5-3mm has a high moisture content, about 1.5%. The highest moisture content occurs in the muck embedded coal, about 2.07%.

The highest ash content comes from the muck which is present mainly in the coal particles greater than 25mm. The coal sample with size of more than 25mm accounts for 20.37% of the 100kg coal sample. Muck and coal embedded muck has been packed in the bigger coal lump, and manually separated, which are weighed and analysed. The muck has sulphur content of 12.15%, ash content of 72%, which can be assigned to pyrite and kaolinite.

The coal embedded in muck has the second highest ash content, 40.37% and sulphur content of 7.89%, which can be understood by considering that it is a mixture of pyrite and coal. The coal in the big lump sample is about 17.96% of the total coal sample. Its sulphur content is about 2.62%, which is very close to that of the coal sample with the size of 0-0.5mm.

Table 2. Analysis of the coal samples with different particle Sizes

Coal size/mm	component	Vd (%)	Content in the overall sample%	Mad/%	Ad/%	Corrected Ad/%	Sulfur/%
>25	coal	14.6%	18.23	1.49	12.40	12.46	2.619
	coal embedded muck	1.6%	1.59	2.07	40.31	40.37	7.892
	muck	0.8%	2.23	1.45	71.16	71.22	12.149
	summary	13.830	22.05	1.53	20.37	20.43	3.965
	25～13	15.5%	13.12	0.95	17.96	18.02	3.613
	13～6	14.5%	23.92	1.23	17.56	17.62	3.736
	6～3	16.5	13.39	1.27	17.48	17.54	2.966
	3～0.5	16.3	18.55	1.48	16.70	16.76	2.799
	0.5～0	15.8	8.97	1.18	21.50	21.56	2.676

The coal sample with the smallest size (0.2-0.5mm) has the lowest ash content, about 15.8%. The sulfur content in the coal component decreases with the coal particle size. The muck lump that was manually separated from the bigger coal lump, which is about 2.23% of the total coal sample has the highest sulfur content, 12.2%, which is from FeS. The coal part with the smallest size has the lowest S content, about 2.67 wt%.

The CHN analysis of the coal with different particle size is given in Table 3. It is interesting to see that the coal with bigger particle size has higher carbon and nitrogen content and relatively lower hydrogen content, except the one with size >25mm which has lower carbon content and also nitrogen and hydrogen content. This can be understood from the table one - there is a significant amount of muck contained in the coal, which is composed of inorganic compounds. These coals may be more mature than the one with smaller sizes.

The crystalline phase in the Luxing coal was identified using X-Ray diffraction, and the results are shown in Fig 1.it is seen that the coal samples have strong diffraction peaks with various diffraction intensities, suggesting the Luxing coal contain lots of crystalline materials. The 2 theta peaks at 12.4, 20.5 and 33.3^o are assigned to the kaolinite, whose formula is $Al_2Si_2O_5(OH)_4$. The diffraction peaks at 26.6^o are assigned to the quartz diffraction, suggesting that the coal has significant amount of quartz. The peaks at 33.3 and 56^o are due to the diffraction of pyrite. The weak diffraction peaks at 29.3^o is due to the dolomite presenting in the coal samples.

In the coal samples with smaller particle size， the peaks of quartz, and kaolinite are relatively weak, while a strong diffraction peaks appear at 29.5, which is due to the presence of dolomite. These results suggest that the different sized coal particles may contain different mineral materials.

Table 3. CHN analysis of the coal samples with different size

Raw coal size range	CHN Elemental Analysis (wt%) C	H	N	H/C mol ratio
	64..51	2.78	1.09	0.53
0.2-0.5mm	67.71	2.64	0.94	0.47
0.5-3mm	60.75	2.63	0.85	0.51
3.-6mm	75.33	2.74	0.98	0.43
6.-13mm	87.81	2.69	1.12	0.35
13.-25mm	81.05	2.51	1.06	0.36
25.-50mm	66.79	2.45	0.87	0.43

It is interesting to see that almost no amorphous phase materials are present in the Luxing coal samples, because no broad lump is seen in the XRD pattern of all the coal samples.

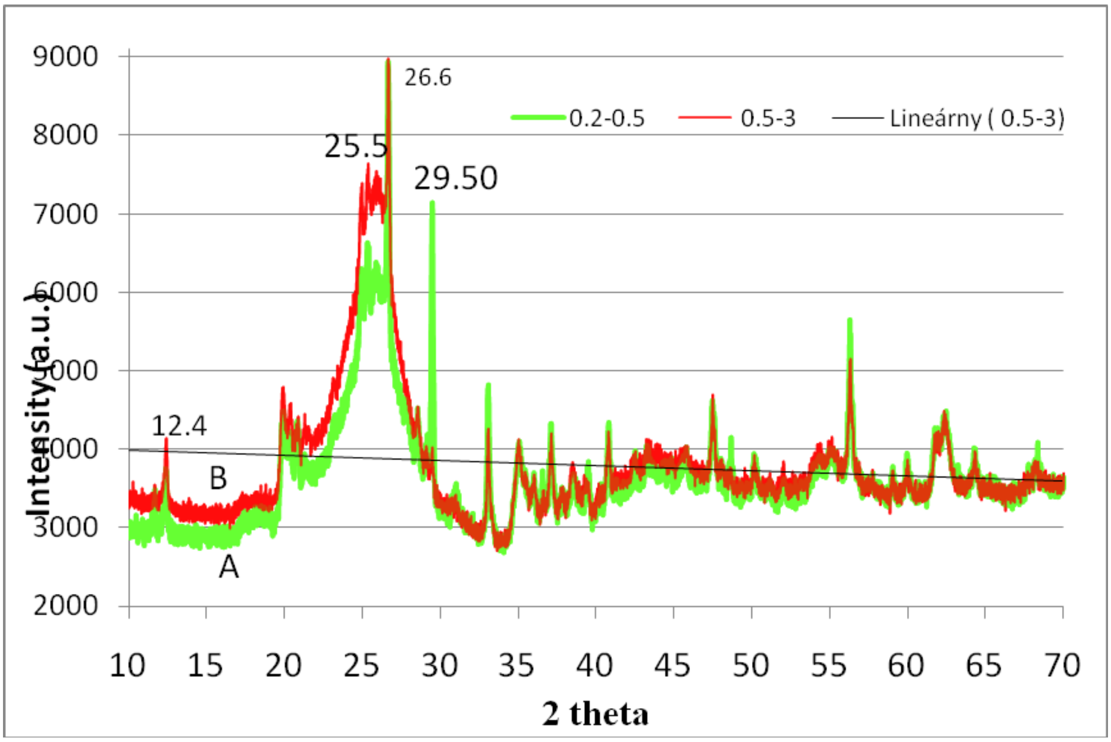


Fig. 2 XRD patterns of the Luxing coal sample with size range of the green 0.2-0.5mm, and red: 0.5-3mm.

Except the strong sharp peaks which are assigned to the inorganic components such as kaolinite, pyrite, quartz, crystoballite, mullite, the strong diffraction peak at 2 theta of 25.8° is due to the crystalline carbon in the coal sample. These results are very different from the coal samples from other reserves [8, 22-26], because normally the coal presents amorphous structure which only show a big broad hump peak at around 24° of 2 theta in the XRD pattern. The Luxing coal shows a relatively sharp peak at 25.6° and a relatively weak peak, which is typical of graphite structure. The peak at 25.6° is the typical (002) plane of graphite, while the one at 45° is assigned to (101).

It has been shown that with coal in the other places [27-29] sometimes the broad peak may be assigned to the minerals, and is due to the high content of the minerals overlapping with weak amorphous coal [29]. In the Luxing coal, clearly the carbon diffraction peak is strong and sharp, although the minerals such as kaolinite, quartz and mullite overlap with it in this position, the crystalline carbon can still be identified. In addition, when the minerals were completely separated using a physical method, this peak become sharp, and more intense, suggesting that the carbon in Luxing coal is in highly crystalline phases, which may be mainly in the graphite phase.

Normally XRD results can give semi quantitative analysis of the crystalline materials in the sample. The stronger diffraction peaks suggests a higher content of the component. The diffraction peaks of kaolinite in the smaller coal fraction, e.g 0-0.5mm, is relatively weak, suggesting it contains less kaolinite than the one with particle size of 0.5-3mm. However, the relative peak intensity of quartz and pyrite in the smallest coal particles is stronger than in the bigger particle (Fig. 5), suggesting that there may exist more quartz and pyrite in the smaller coal size. Also strong diffraction peaks appear at 29.6 and 48.1 in the diffraction patterns of the coal sample with the size of 0.2-0.5, which are assigned to the dolomite. The reason for the coal sample with the smaller particle size having high content of dolomite is that the dolomite may be finely present in the coal layer, which exist as fine powder in separate phase, as it is easily sieved out from the total coal sample.

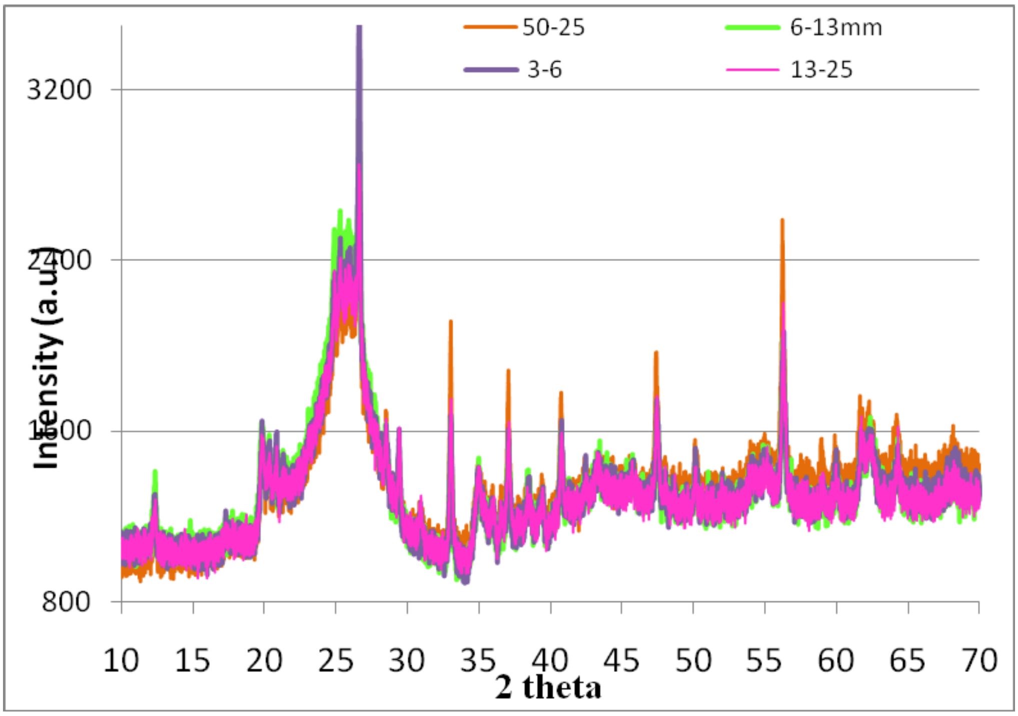


Fig. 3: XRD patterns of the Luxing coal sample with bigger size range

In the coal samples with bigger particle size range, XRD showed that the coal sample with 3-6mm particle size range has the highest quartz content, but relatively low mullite, dolomite and kaollinite and pyrite. In the sample with the particle size range of 6-13mm, there are more kaolinite and mullite, crystallite, but less quartz and pyrite. The sample with particle size of 13-25mm has the lowest impurities such as quartz, kaolinite and pyrite. Clearly, the sample with particle size larger than 25mm has the highest mullite and pyrite, which is in agreement with the elemental analysis, as shown in table 1.

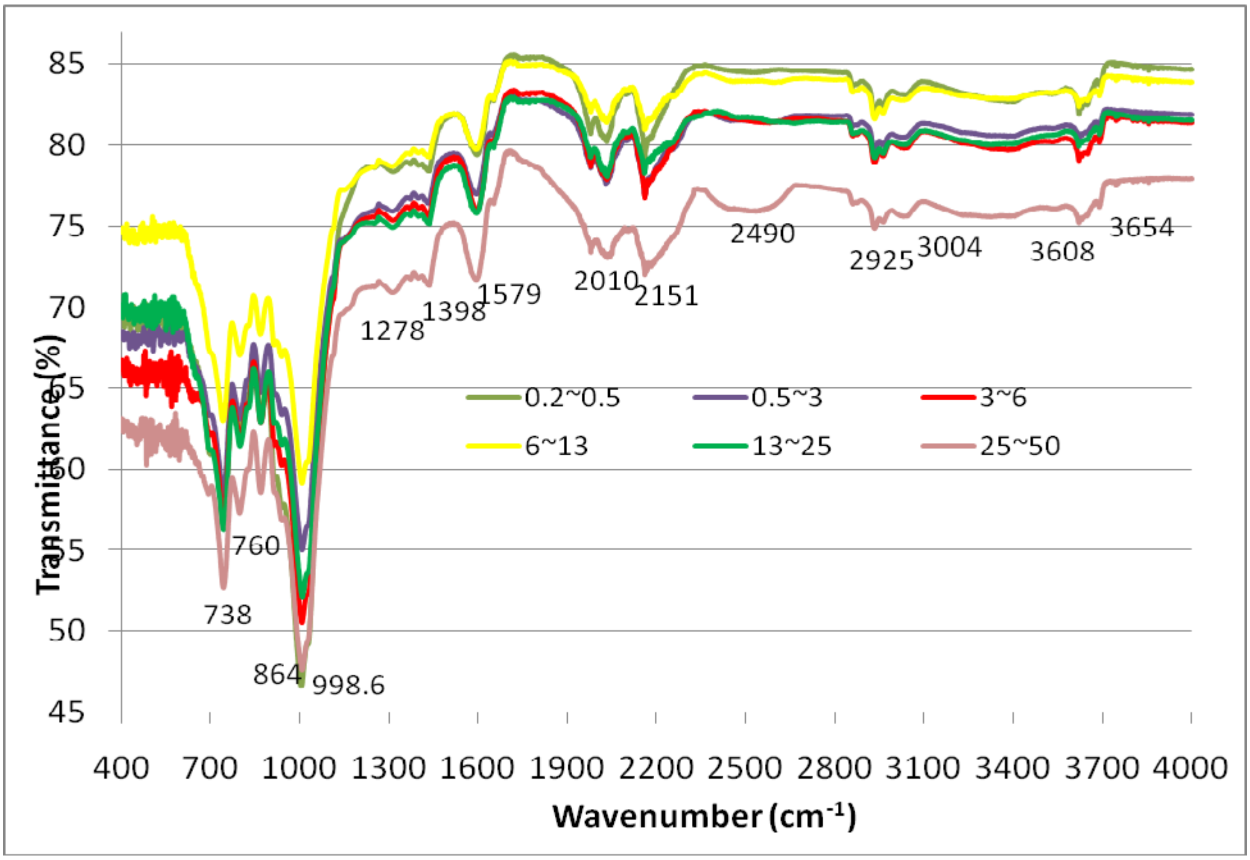


Fig. 4. FT-IR spectrum of the coal sample with different particle sizes

The FT-IR data obtained from coal samples of different sizes are shown in Fig. 4. All the coal samples show IR transmission bands at 998, 864, 760, and 481 cm^{-1} and a shoulder at 1018 cm^{-1}, which is assigned to the to the oscillation vibration of Si-O-Si in quartz and kaolinit, and the strong peak at 998 and 738 are assigned to the C=O vibration in dolomite ($CaMg(CO_3)_2$)[30], i.e., dolomite. The peaks at 2010-2151cm^{-1} are due the oscillation valence of the Ar-H, and Ar-OH. The peaks at 2925-3004 cm^{-1} are due to the C=O bonds in the coal, and the peaks. The peaks 3608-3654cm^{-1} are due to the Ar-H stretching vibration [30-32].

The intensity of peak at 2920 cm$^{−1}$ is greater than the peak 2850 cm$^{−1}$ indicating the presence of long aliphatic chains in the coal. . The peak around 1579 cm$^{−1}$ in the coal is observed due to aromatic C=C, vinylic C=C and possibly due to other O-containing functional groups. The oxygen containing functional groups found in coal specifically include phenols and alcohols, ethers, carboxylic acid and carbonyls. In view of the diversity of decomposed plant matter, finding any systematic variation in the distribution of these functional groups in coal seems unlikely. Several authors have reviewed quantitative determination of these various oxygen functional groups. . The band at 1398 cm$^{−1}$ is mainly due to CH_3 symmetric deformation while $–CH_3$ and $–CH_2$ in cyclic structures may also partly contribute to this band.

The band between 864 cm^{-1} and 738 cm$^{−1}$ has been assigned to aromatic structures [33]. The weak band at 670 cm$^{−1}$ observed in the coal could possibly be due to C–S bond. These absorptions are useful in determining the aromatic ring structure of a coal.

It is very interesting to see that the relative peak intensity of 1018cm^{-1} in all the samples does not differ greatly, suggesting that there have been equivalent amounts of quartz and kaolinite. The peak intensities of 998.6cm^{-1} and 738cm^{-1} decrease as the coal particle size increases, suggesting that the dolomite content increases as the coal particle size becomes smaller.

Although the pyrite has been detected by XRD, it has very weak vibrations which normally appears at 400-600cm^{-1}, and due to the strong vibrations of the other minerals such as kaolinite, dolomite and mullite, the IR absorption is not seen.

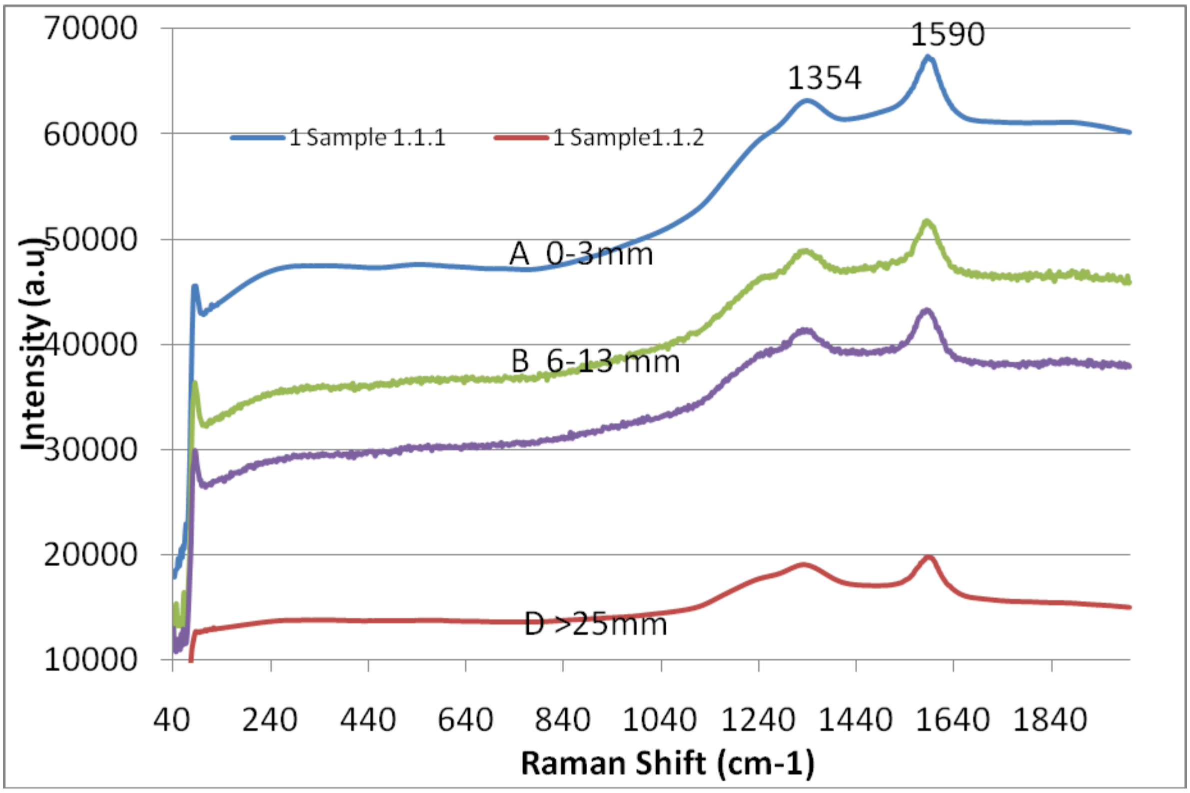


Fig 5. Laser Raman spectra of Luxing coal sample with different particle size.

The coal samples with different particle sizes were measured with Laser Raman spectroscopy, and the results are shown in Fig. 5. Laser Raman spectroscopy has been applied to structural characterization of carbon materials including graphite and glassy carbons [34-36], but polycrystalline graphite and carbon materials show another Raman band at 1360 cm-^{1}.

The 1360 cm^{-1} band has been assigned to a vibrational mode originating from the distorted hexagonal lattice of graphite near the crystal boundary [5], and can therefore be observed for ordinary carbon materials containing various defective structures in the graphite layer planes, i,e. a defect induced Raman vibrational mode. It has been reported that the relative intensity ratio of the 1360 cm^{-1} band to the 1580cm^{-1} graphite band increases on going from natural graphite through polycrystalline graphite up to glassy carbon [34], and can be used as a measure of imperfection of the graphite layer planes [36]. Because laser Raman is based on surface scattering technology and the coal samples with various sizes are covered with the carbon, only two main bands are seen in all samples. These bands are seen at 1354cm^{-1} and 1590cm^{-1}. The intensity of the peak at 1354cm^{-1} stays almost the same across all samples, while the peak at 1590cm^{-1} increases with the coal particle size decreasing. As reported in the literature, the crystalline ordered carbon shows the G band at 1560cm^{-1}, while the band at 1354cm^{-1} is mainly the defected crystalline or deformational plane of the carbon. The laser Raman results showed that the Luxing coal has crystalline carbon presenting in the sample. The coal fractions with the smaller particle size have the higher crystallinity, i.e. more graphite is present in the smaller coal particles.

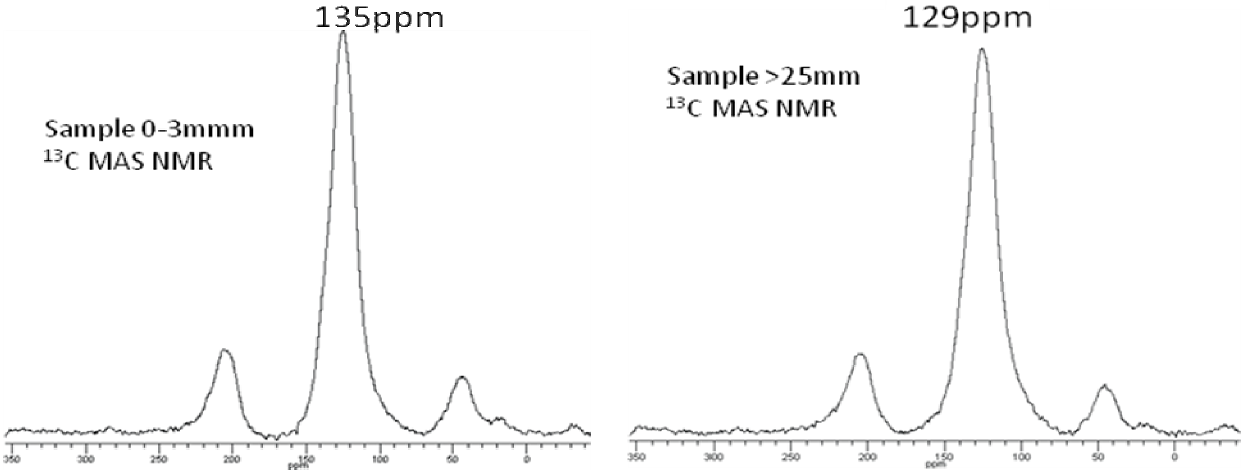


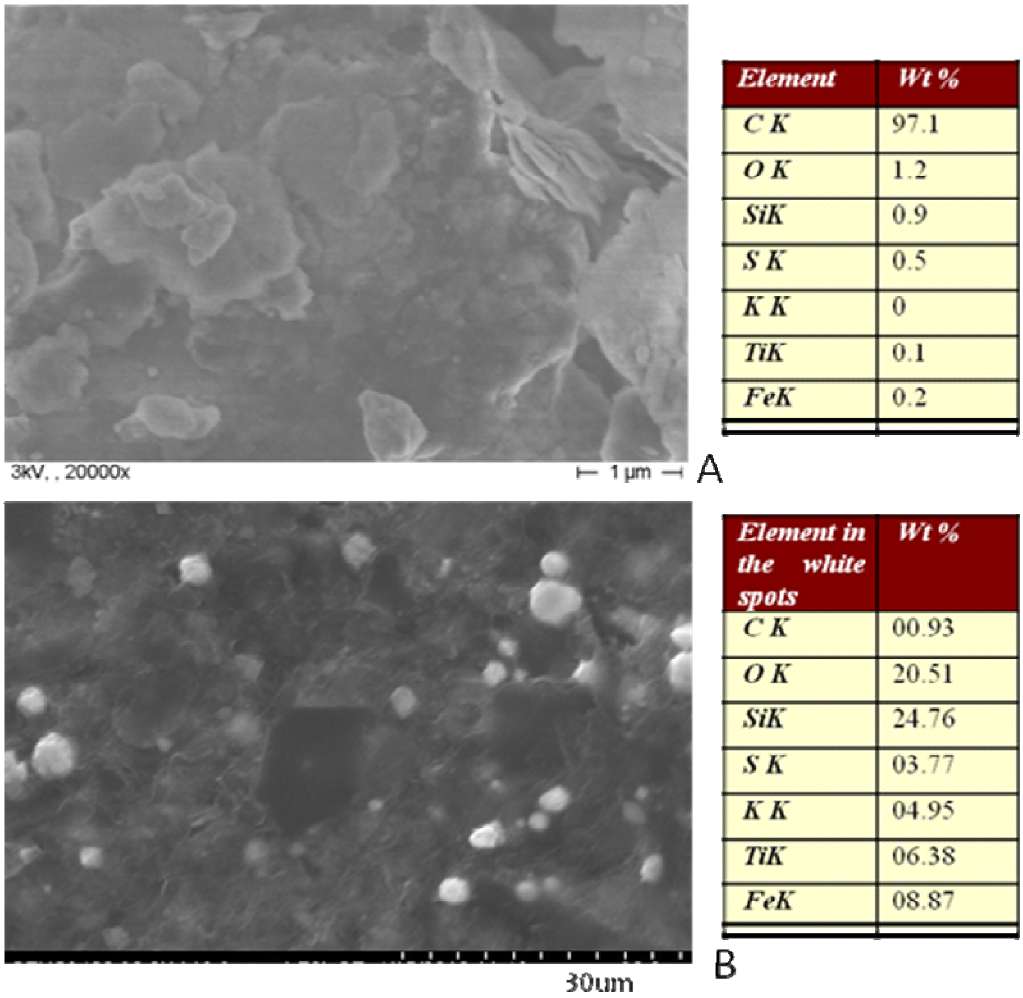
Fig. 6. ^{13}C MAS NMR of the coal samples with different particle sizes

Solid state ^{13}C MAS NMR spectroscopy offers the advantage that spectra can be acquired on whole coal samples with little or no pre-treatment [6, 37, 38]. To further study the carbon status in the coal samples with various particle sizes, ^{13}C NMR measurement was carried out for the samples with particle size of 0-3mm and >25mm. Three main NMR bands are observed in all the samples, one at about 18 -50ppm, the main band at 135ppm, and the third at the chemical shift peaked at 205ppm. Normally the peaks at the chemical shift of NMR at (0–50) ppm region are assigned to the aliphatic carbons in the sample [39-43]. The peak centred at 130ppm above is normally due to the aromatics. Graphite is a mature polyaromatic, which normally has chemical shift at 135-138ppm. The broad ^{13}C NMR bands at 200ppm above are due to the carbon atoms in the carboxylic or ketonic compounds.

Normalization of the ^{13}C NMR showed that the peak at 135ppm is about 87% of the total components, the aliphatic carbon accounts for 4.1%, and the carboxylic and ketonic carbons account for 8.9%.

In the sample with the particle size greater than 25mm, three similar major ^{13}C NMR bands are observed; the aliphatic carbon NMR signal is relatively weaker than the one with smaller size, while the aromatic carbon peaks at 130ppm, which is less mature and crystallized than that seen in the sample with smaller particle size. Also peaks assigned to carboxylic and ketonic carbons have more or less the same intensity. Comparing Fig. 6 a and b showed that the coal sample with smaller particle size has higher chemical shift, 135ppm while the one with bigger particle size has ^{13}C NMR band at 130ppm, suggesting it has more graphite. Also the aliphatic carbon content is about 5.8%, and the ketonic carbon content at around 200ppm is about 9.6%.

The SEM-EDX results of the coal sample with the size of 0-3mm are shown in Fig. 7. It is seen that the samples are not very uniform, some points are rich in carbon, and at some points the minerals co-exist with the carbon materials. Fig. 7-A shows that the carbon rich area, which has more than 97% of carbon, has few mineral impurities except a small amount of Si and oxygen. The morphology of the materials shows a layer-like structure, which is characteristic of graphite. This further suggests that graphite is present in Puan coal. However, in other domains of the coal sample there are white dots observed in the SEM images. These were analysed using EDX, and the composition of the white sphere showed a much higher silica, iron and titanium content. This suggests that the mineral particles are not trapped in the coal later, which may be easily separated using physical methods. However, on the mineral free region, the dark area, the main component is carbon, with small amounts of sulphur present, which suggests that organic sulphur is present in the graphite layer.



Element	Wt %
C K	97.1
O K	1.2
SiK	0.9
S K	0.5
K K	0
TiK	0.1
FeK	0.2

Element in the white spots	Wt %
C K	00.93
O K	20.51
SiK	24.76
S K	03.77
K K	04.95
TiK	06.38
FeK	08.87

Fig. 7 SEM-EDX results of the coal sample with the size of 0-3mm

4. Conclusion

The Luxing coal in Puan County, Guizhou Province China has been sampled and sieved to different particle sizes. The properties and composition of the coal sample with different sizes have been characterised using elemental analysis, XRD, FTIR, 13C Solid State NMR and Laser Raman spectroscopy. The results are as follows:

1. Luxing coal is mainly anthracite coal with heating value more than 30kJ per gram, and average coal content more than 3wt%.
2. The coal with bigger particle size (> 25mm) has the high muck content, which is mainly pyrite. This coal has high ash content and sulphur content, although it has a higher commercial price in the local market. The coal with smaller size has less sulphur and relatively low ash content except the sample with the smallest size, 0.2-0.5mm.
3. The main minerals in the coal samples include kaolinite, quartz, mullite, dolomite and pyrite. The pyrite is mainly present in the coal with the bigger particles. Kaolinite and quartz are present in all the coal samples with various sizes. The coal sample with small size has higher dolomite content.
4. The carbon component in the Luxing coal sample is highly crystallized, which is semi-graphite or graphite material. The coal with the smallest size has more graphite-like

materials, which is about 90% of the carbon. The other carbon in the coal also include aliphatic carbon and carboxylic and ketonic carbon materials that account for more than 15% of the carbon materials

5. It is recommended that the Luxing coal should be further treated to separate the mineral and treat the coal to graphitification of the resources.

Acknowledgements

We are grateful for the financial support of Ministry of Science and Technology, and the Collaboration project between China-ICUK. Thanks are also due to the Luxing Coal Reserve Company and the Guizhou Provincial Science and Technology Department for their support. Tiancun Xiao would like to express his sincere thanks to Chaoyun Long, and the Guizhou Provincial Government for their care and helps in the projects.

References

[1] Fan, W. and Y. Zhang: Chinese coal industry - gearing up for the 21st century. Journal of Mines, Metals and Fuels, 1997. 45(11&12): p. 321-325.

[2] Ghose, M.K.: Technological challenges for boosting coal production with environmental sustainability. Environmental Monitoring and Assessment, 2009. 154(1-4): p. 373-381.

[3] Mishra, U.C.: Environmental impact of coal industry and thermal power plants in India. Journal of environmental radioactivity, 2004. 72(1-2): p. 35-40.

[4] Radjenovic, A.: Inorganic constituents in coal. Kemija u Industriji, 2006. 55(2): p. 65-71.

[5] Davis, B.H.: Clean fuels from coal: The path to 1972. Prepr. Symp. - Am. Chem. Soc., Div. Fuel Chem., 2003. 48(1): p. 141-143.

[6] Gupta, R.: Advanced Coal Characterization: A Review. Energy Fuels, 2007. 21(2): p. 451-460.

[7] Saikia, B.K. and R.K. Boruah: Structural studies of some Indian coals by using X-ray diffraction techniques. J. X-Ray Sci. Technol., 2008. 16(2): p. 89-94.

[8] Saikia, B.K. and R.K. Boruah: X-Ray Structural Analysis Of Some Indian Coals. AIP Conf. Proc., 2009. 1202(Neutron and X-Ray Scattering in Advancing Materials Research): p. 112-116.

[9] Yang, J.: Modes of occurrence and origins of noble metals in the Late Permian coals from the Puan Coalfield, Guizhou, southwest China. Fuel, 2006. 85(12-13): p. 1679-1684.

[10] Onodera, J., et al.: Results of the demonstration operation, the demonstration and dissemination project for a coal preparation system, model project for an environmentally harmonized coal utilization system in China. Coal preparation technology suited for de-sulfurizing and de-ashing performance. Shigen to Sozai, 2003. 119(4,5): p. 214-219.

[11] Yang, J., Concentrations and modes of occurrence of trace elements in the Late Permian coals from the Puan coalfield, southwestern Guizhou, China, Environmental Geochemistry and Health, 2006. 28(6): p. 567-576.

[12] Yang, J.: Concentrations and modes of occurrence of trace elements in the Late Permian coals from the Puan Coalfield, southwestern Guizhou, China, Environmental geochemistry and health, 2006. 28(6): p. 567-76.

[13] Belkin, H.E. and K. Luo, Late-stage sulfides and sulfarsenides in Lower Cambrian black shale (stone coal) from the Huangjiawan mine, Guizhou Province, People's Republic of China. Mineralogy and Petrology, 2008. 92(3-4): p. 321-340.

[14. Han, G. and C.-Q. Liu, Water geochemistry controlled by carbonate dissolution: a study of the river waters draining karst-dominated terrain, Guizhou Province, China. Chemical Geology, 2004. 204(1-2): p. 1-21.

[15] Han, G. and C.-Q. Liu: Strontium isotope and major ion chemistry of the rainwaters from Guiyang, Guizhou Province, China. Science of the Total Environment, 2006. 364(1-3): p. 165-174.

[16] Jiang, Y.-k., C.-q. Liu, and F.-x. Tao: Sulfur isotope composition characters of Wujiang river water in Guizhou province. Shuikexue Jinzhan, 2007. 18(4): p. 558-565.

[17] Lang, Y.-c., et al.: Chemical compositions of surface and ground waters of Guiyang city: discussion of water-rock interaction and contamination in karstic hydrological system. Shuikexue Jinzhan, 2005. 16(6): p. 826-832.

[18] Liu, D., et al., Investigations on characteristics of organic matter from Keweenaw-like-type copper mine along Yunnan-Guizhou geochemical boundary and implications for ore-formation conditions. Dizhi Lunping, 2006. 52(4): p. 477-485.

[19] Xu, Z. and C.-Q. Liu: Chemical weathering in the upper reaches of Xijiang River draining the Yunnan-Guizhou Plateau, southwestern China. Chemical Geology, 2007. 239(1-2): p. 83-95.

[20] Zhao, Y., et al.: Arsenic emission during combustion of high arsenic coals from Southwestern Guizhou, China. Energy Conversion and Management, 2008. 49(4): p. 615-624.

[21] Zhu, B.-z., Y.-l. Sun, and C.-W. Xie: Spectroscopy research on the Guizhou Xingyi gangue of different calcined temperatures. Meitan Xuebao, 2008. 33(9): p. 1049-1052.

[22] Saikia, B.K., R.K. Boruah, and P.K. Gogoi: FT-IR and XRD analysis of coal from Makum coalfield of Assam. J. Earth Syst. Sci., 2007. 116(6): p. 575-579.

[23] Saikia, B.K., R.K. Boruah, and P.K. Gogoi: XRD and FT-IR investigations of sub-bituminous Assam coals. Bull. Mater. Sci., 2007. 30(4): p. 421-426.

[24] Saikia, B.K., R.K. Boruah, and P.K. Gogoi: X-ray (Radial Distribution Function, RDF) and FT-IR analysis of high sulphur Tirap (India) coal. J. Energy Inst., 2009. 82(2): p. 106-108.

[25] Saikia, B.K., R.K. Boruah, and P.K. Gogoi: A X-ray diffraction analysis on graphene layers of Assam coal. J. Chem. Sci. (Bangalore, India), 2009. 121(1): p. 103-106.

[26. Taneja, S.P., M.P. Aggarwall, and A.S. Brar: Hyperfine and x-ray studies of coal and coal ash. Nuclear Instruments & Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms, 1993. B76(1-4): p. 236-8.

[27] Bi, H.: X-ray diffraction characteristics of Ceshui Formation coal in Lianyuan coal basin, China. Chinese Journal of Geochemistry, 1998. 17(2): p. 170-174.

[28] Liu, G., et al.: Depositional and chemical characterization of coal from Yayu coal field. Energy Explor. Exploit., 2006. 24(6): p. 417-437.

[29] Wang, W., et al.: Partitioning of minerals and elements during preparation of Taixi coal, China. Fuel, 2005. 85(1): p. 57-67.

[30] Painter, P.C., et al.: Analysis of kaolinite in coal by infrared spectroscopy. Fuel, 1980. 59(5): p. 364-6.

[31] Landais, P. and A. Rochdi: Reliability of semiquantitative data extracted from transmission microscopy-Fourier transform infrared spectra of coal. Energy Fuels, 1990. 4(3): p. 290-5.

[32] Urbanski, T., et al.: The infrared absorption spectra of extracted coals. Bull. Acad. Pol. Sci., Ser. Sci., Chim., Geol. Geogr., 1959. 7: p. 207-14.

[33] Shishkov, G. and R. Petrova: Infrared spectra of coal macerals separated from Bulgarian lignites. Fuel, 1974. 53(4): p. 236-9.

[34] Friedel, R.A. and G.L. Carlson: Laser Raman spectral investigation of coals. Chem. Ind. (London), 1971(40): p. 1128-9.

[35] Nakamizo, M., R. Kammereck, and P.L. Walker, Jr.: Laser Raman studies on carbons. Carbon, 1974. 12(3): p. 259-67.

[36] Rellick, G.S.: Carbon and graphite matrixes in carbon-carbon composites: an overview of their formation, structure, and properties. 1992, Mech. Mater. Cent., Aerosp. Corp., El Segundo, CA, USA. p. 41 pp.

[37] Kumar, M. and R.C. Gupta: Graphitization study of Indian Assam coking coal. Fuel Process. Technol., 1995. 43(2): p. 169-76.

[38] Saito, K., K. Kanehashi, and I. Komaki, Applications of NMR techniques to coal science. Annu. Rep. NMR Spectrosc., 2001. 44: p. 23-74.

[39] Hu, J.Z., et al.: Structural determination in carbonaceous solids by using advanced solid state NMR techniques. Energy Fuels, 2001. 15(1): p. 14-22.

[40] Pugmire, R.J., et al.: Applications of the 13C NMR magic angle turning experiment to coal studies. Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem., 1995. 40(3): p. 411-14.

[41] Pugmire, R.J., et al.: Applications of the 13C NMR magic angle turning experiment to the study of coals. Coal Sci. Technol., 1995. 24(Coal Science, Vol. 1): p. 335-8.

[42] Sharma, D.K. and S. Mishra: Carbon-13 NMR spectral studies of the depolymerized coal obtained by acidic phenolation. Fuel Sci. Technol. Int., 1990. 8(4): p. 351-77.

[43] Havens, J.R., et al.: Characterization of coals and coal oxidation by magic-angle carbon-13 NMR spectroscopy. Fuel, 1983. 62(8): p. 936-41.