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A Total Analysis of a Kentucky Coal: ^{1}H by VCT CRAMPS; ^{13}C by CPMAS NMR Minor Constituents by Spectroscopy using an Inductively Coupled Plasma

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ABSTRACT

The average chemical functionalities of hydrogen and carbon, inferred by high resolution Nuclear Magnetic Resonance (NMR) of a solid coal, were determined via NMR of ^{1}H utilizing Variable Cycle Time CRAMPS [1], and from NMR of ^{13}C utilizing CPMAS [2, 3]. Concentrations of the minor constituents As, Hg, Pb, and U, were determined from emission spectra of these species in an Inductively-Coupled Plasma [4].

Keywords: Analysis of a Kentucky Coal.

INTRODUCTION

While there have been many reports on the use of NMR of ^{1}H and ^{13}C of solid coals [5 - 13], to our knowledge, there no analyses of solid coals utilizing Variable Cycle Time- Combined Rotation and Multiple Pulse Spectroscopy [14] on ^{1}H, in which the protons in the rigid portion of the coal matrix are detected under conditions of relatively high resolution, and those in the mobile portion are detected, to better than 0.01 wt-% when the multiple-pulse cycle time of the dipolar decoupling sequence used, in this case the MREV-8 pulse sequence [15,16] in which the cycle time, t_c of the multiple pulse sequence used for averaging the homogeneous dipolar coupling to zero must be shorter than the inverse of the dipolar line width [17]. In this case, when the amount of relatively mobile phase is sufficiently relatively small, e.g. $\leq$ 0.1 wt.-percent, the mobile portion is immersed in the noise, and is not detected. On the other hand, when the cycle time, t_c is greater than the inverse of the dipolar line width of the solid, but less than the dipolar – broadened line width of the more mobile fraction, the dwell time of the experiment is such that the time decay of the signal from the rigid portion is over before an observation, and acquiring a suitable number of time averages of the signal compared to those used in obtaining NMR of the rigid portion, only the more mobile fraction is detected quantitatively. It is important to note that protons in the polyflon ™ capacitors in the NMR probe, are *not* detected, because the averaging of the homonuclear dipolar interactions takes place only within the inductor of the probe. One must take care to utilize dry air or nitrogen to drive the rotor for MAS, however, because on relatively humid days, protons in the atmosphere may be detected.

MATERIALS AND METHODS

The coal studied was from the Dodge Hill Mine, in Union County Kentucky. NMR of ^{1}H and ^{13}C were measured utilizing a Bruker Avance ™ spectrometer operating at a resonance frequency of 600 MHz for protons with a triple-resonance probe with a 4 mm diameter rotor. NMR of protons were measured under (a) a single pulse excitation, spinning at 25 kHz at the magic angle (b) The spectra under Variable Cycle Time Combined Rotation And Multiple Pulse Spectroscopy (VCT CRAMPS), the cycle times, t_c for the MREV-8 sequence [18] were varied between 36 μs and 288 μs. At t_c = 36 μs only the protons in the relatively rigid portion of the sample are detected, the protons in the relatively mobile portion being at sufficiently low concentration ,in this case, as shown in table 1, 0.058 wt.-%, that the signal associated with these is buried in the noise. At t_c = 36 μs, the number of scans was 64. At t_c = 288 μs , the number of scans was 4,000.

Emission spectra from an ICP plasma were measured with an Agilent 4500 ICP-MS. The Standard reference materials are from Plasmachem Associates, Inc. The microwave digestion system is CEM-corporation MDS-2100. Two methods were used to measure concentrations of As, Hg, Pb and U: (i) the samples were immersed in HNO_3 which did not completely dissolve them. In this process, the metals are leached from the coal, but the silicates are not completely dissolved. (ii) HNO_3 + HF completely dissolved the samples. The concentrations obtained using the second method were six to ten times higher than those obtained in the first, so these results are considered more reliable.

RESULTS AND DISCUSSION

Table 1 exhibits the results of the NMR of ^{1}H and ^{13}C detection of ^{1}H and ^{13}C in the various portions detected in the sample studied. The intensities in many samples of the same piece of this coal vary by ≤ 10%. $I^{k}(A,j)$ is the relative intensity of the kth component of element A in state j.

TABLE 1

I^{tot} (13 C, s)	$I^{AR}(^{13}C,s)$	$I^{AL}(^{13}C, s)$	$I^{AR}(^{1}H, s)$	$I^{AL}(^{1}H,s)$	$\underline{I^{mobile}(^{1}H)}$
0.250	0.150	0.089	0.031	0.672	0.080

Keeping in mind that the ratio of aromatic hydrogen to aromatic carbon in benzene, C_6H_6 is unity, and for naphthalene, $C_{10}H_8$ is 0.8, and decreases with the size of the aromatic rings, we infer from table 1, taking into account the natural abundance of ^{13}C, which is 1.01 relative to 99.98 for ^{1}H, that the ratio of aromatic hydrogen to aromatic carbon is 0.023, indicating that this coal is quite aromatic, indeed. Again, the ratio of aliphatic hydrogen to aliphatic carbon is 0.09, indicating that the coal is not at all aliphatic, in agreement with the inference that the coal studied is relatively highly aromatic.
Analyses for the elements As, Hg, Pb, and U via emission spectroscopy utilizing an ICP are given in table 2.

TABLE 2

Element	As	Hg	Pb	U
Conc./ppm	0.451	0.282	9.24	2.95

The first carcinogen to be detected was a component of soot from coal-fire places in England [11]. Young Chimney Sweeps were contracting cancer of their scrota, because that portion of the body was where the skin was moist and the benzo-a[pyrene] contained in the soot was most efficiently absorbed. In addition, of

course, the poisons As, Hg, Pb and U were undoubtedly present in concentrations of ppm (table 2) to add insult to injury.

The present results indicate that unless appropriately cleaned, an effort strongly opposed by the G.W. Bush administration and leading to roughly 300 deaths a year in the state of Iowa, about 20,000 deaths a year in the continental US, and about a million deaths a year in China [20, 21] coals are just too dangerous to use as a source of energy. In addition, the use of algae to produce oil [22], the use of solar [23] and wind [24] to generate electricity, and the global climate crisis all dictate that alternate sources of energy be tapped to produce power for electricity and for transportation. Further, as reported by David Duprey, of the Associated Press, on Feb. 22nd, 2009, seventy five coal miners in China were killed in a mine accident. The bulletin states "China's state media said that at least 74 miners were killed Sunday after a gas explosion ripped through a coal mine in the northern part of the country. Dozens may still be trapped in the shaft. Here, rescuers carry a body at the facility in Gujiao city near Taiyuan, the capital of Shanxi province.The story continues: China's mines are the world's most dangerous with more than 3,000 deaths a year in fires, floods and explosions.
The pre-dawn blast occurred while 436 workers were in the Tunlan Coal Mine in Gujiao city near Taiyuan, the capital of Shanxi province, the official Xinhua News Agency said.
At least 74 miners died and 114 others were hospitalized, including six in critical condition, Xinhua said. It did not say how many workers remained trapped in the shaft but earlier reports said 65 were still underground.
Most of the injured miners were suffering from carbon monoxide poisoning, Xinhua said, citing doctors at a nearby hospital. Exposure to carbon monoxide, an odorless, colorless gas, can lead to death.
Xinhua said about 80 rescuers were searching for survivors.
State television CCTV showed rescuers in orange suits and red helmets with headlamps entering an elevator to be lowered into the mine shaft, while others emerged from the mine carrying workers on stretchers toward waiting ambulances.
A rescuer said in a phone interview with CCTV that some sections of the mine remained inaccessible to emergency teams because of high levels of carbon monoxide.

APPLICATIONS

The Analysis of Coal is useful to know about Pollution levels.

CONCLUSIONS

The coal analyzed in this work, at least, is dangerously contaminated with carcinogens. There is no way to safely utilize such a fossil material to generate electrical power. Either the emissions from the stack will kill people living downwind of the power plant, or the poisons in the ash, some of which are radioactive, without proper disposal [25], will result in injury and death to those coming in contact with this poisonous material. Given the ready availability of environmentally friendly, and non polluting generation of oil, electricity, and hydrogen for use in power plants and transportation, there is no reason, other than further profits for the so-called "Energy Companies", to continue tearing off mountain tops in Appalachia, and polluting the water used by the Hopi and Navaho native populations in the vicinity of Black Mesa [26].

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[24] Iowa is the second largest producer of electricity from wind in the US, behind Texas, and ahead of California. Contact *The Iowa Energy Center*, 2521 University Blvd, Suite 124, Ames, Iowa, USA, 50010-8229.

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