

Semi Critical Assisted-Solvent Extraction: A Highly Thermochemical Technology For Hydrocarbon and Organic Associate Minerals Extraction In Bituminous Coal

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ABSTRACT

The extraction of raw material (gas, hydrocarbon) and hazard contaminants (ash, heavy metals, poly-aromatic hydrocarbons, organic associate minerals, OAM) from bituminous and lignitic coal, are challenge processes in regards of adding economical value at coal energy content. Supercritical fluid extraction, **SFE** (high pressure/temperature dependent) and modified Soxhlet, **Sx** (solvent density dependent) technologies had dominated organic and associated minerals extraction on coal for long time ago, however parallel methods till shows similar results as those obtained with these technologies, so new methods to address the short stage for hazard contaminants extraction are highly in needs. Improvements in a highly thermochemical method termed *semi critical assisted-solvent extraction (SmCA-S)* is reported herein, which applies for a broad scope of technological, scientific, and academic fields in regards of extract/separate biodiesel, ash, metal ions, and polyaromatic hydrocarbon from different kind of sources. Therefore, an innovation has been designed to carried out SmCA-S experiments, which we hypothesize works to generate a laminar flow, with the fluid being composed by a biphasic state (gas/liquid) that coexists in isothermal equilibrium. The novel aspect of the innovation is related with facile operation, less time and solvent consume, and most important *in situ* thermodynamic property measurements (temperature, polarity, pressure, pH), impossible to be determinate either using Soxhlet, Gregar or Soxtec glassware extractors.

Keywords: Coal, Percolation, Critical Extraction, Assisted-Solvent Extraction, Soxhlet

1. INTRODUCTION

The high levels of environmental contaminants than in soil and the atmosphere, is largely associated with the incomplete combustion and pyrolysis of organic matter from natural or anthropogenic sources (e.g. forest fires, volcanic eruption, cars emissions, house-wood burning), as well as by industrial combustion of fossil fuels such as petroleum catalytic cracking and coal-assisted pyrolysis.

Coal is the second largest source of fuel in the world, and the most common fossil fuel employed for utility and power generation. Coal however, is compose by heterogeneous materials with a wide variety of ranks which dependent on

where it falls in the coalification process, therefore, a careful analysis on its chemical content is necessary to determine its risks as a commodity, with deep environmental impact decreases its economic benefits.

Especially, the high content of associated minerals in low rank bituminous coal (the most used for power generation) is associated with health concerns like mutagenic and/or carcinogenic properties. Nevertheless, an increased interest in the extraction of coal environmental contaminants such as poly-aromatic hydrocarbons, asphaltene, ash, and minerals utilizing conventional assisted-solvent and improved thermic technologies has been moderately covered in the past twenty years. In this regards special attention has been pay to critical and supercritical fluid methods because the enhanced solubility of substrates in the fluid phase that occurs at or above the solvent critical point, which can be conveniently controlled over a large range of experiments with little changes in the solvent's pressure or temperature [1]. Sub-bituminous coal contain high levels of organically associated elements such as Na, K, Mg, Ca, Al, and Sr in addition to other mineral grains, which are present as salts of organic acid groups [2].

Unlike lower-rank coals, the inorganic components in bituminous coals consist mainly of discrete mineral grains with very minor amounts of organically associated elements. In this paper, SmCA-S was applied for the extraction of organically associated minerals from a Canadian bituminous coal to compare its reliability with a long time technology (Soxhlet) when carried out under similar conditions.

High field scanning electron microscopy (FESEM) and EDS techniques were used to analyze organically associated minerals content, coals surface morfology among carbon, oxygen, and chlorine composition on crude and treated coals [3]. The FESEM-EDS method was found to be a valuable analytical tool because it provides a means for acquiring single-particle trace element data by mapping different coal areas, an information that is essential to understand how extraction technologies can be improved in regards of control the emission of organic pollutants and trace elements during fosil fuels combustion.

2. EXTRACTION TECHNIQUES COMPARISON

2.1 Soxhlet Extraction: Soxhlet extraction method has been used as the benchmark technique in the extraction of oils, folk medicines among poly-aromatic hydrocarbons from coals, soils and sediments. Briefly, in the Soxhlet extraction method, a grinded sample is poured into an extraction thimble, which is then extracted using an appropriate solvent via continuous reflux cycle system. The boiling solvent creates a vapor phase, which passes through a bypass arm into the condenser vessel where it condenses and drips back onto the sample inside the thimble. As the solvent reaches the top of the siphon arm, the mixture (solvent/extract) is siphoned back onto the lower reaction flask whereby the solvent reboils and the cycle is repeated until all extracted material is recovered in the reaction flask.

One of main disadvantages of this extraction method deals with the use of large volumes of solvent, which usually are more than 150 mL to handle as little as 10 g of coal sample. In addition, the method is very labour intensive and time consuming, as the solvent needs to reflux up to 24 hours to achieve considerable extraction efficiencies. Former studies on soil sample extraction showed that chromatograms of extracts using GC-MS and GC-FID yielded more artifact peaks, which corresponds to n-alkanes and humic substances among poly-aromatic hydrocarbons, which were extracted using the Soxhlet technique [4, 5]. Other concerns using Soxhlet extractor include the likelihood of sample carryover, the need to fractionize extracts to avoid heavy contamination of GC injection port, and the unfeasibility of re-dissolving dried extracts clogged inside the siphoning pipe [6].

2.2 Semi Critical Assisted-Solvent Extraction, SmCA-S:

Liquids and gases share two intensive properties (density, δ and viscosity, ρ), which are directly related to their fluidity and velocity inside a transporting system. However, a gas is more fluid than its original liquid and then, its viscosity, which is defined as *the resistance that a part of the fluid shows to the displacement of the other*, controls the process.

Viscosity, ρ is therefore produced by the cutting effect of a layer of fluid when it is being displaced over other and is completely different than the so-called intermolecular attraction. Assuming that a liquid stratifies in molecular planes, the area of one plane is defined as A and the inter-planes distance as dy . Similarly, one can assume that each plane in the flow moves to the right with velocities v_1, v_2 , etc., where each value is greater than its predecessor by the increment dy . Therefore, the flow occurring according to this pattern is called *laminar* and is different than the so-called *turbulent* where plane parallelism is not observed (as occur in SFE). Hence, in the SmCA-S method is hypothesized that it occurs like a laminar flow, with the fluid phase being composed by almost two different states (liquid/vapor) but coexisting in equilibrium isothermal.

Under this stage of equilibrium, the binary fluid possesses the required force to maintain a stationary velocity difference dv between the two parallel planes, which is directly proportional to A and dv but is inversely proportional to dy , according with the relationship:

$$f = \eta A [dv] dy; f = \eta A [dv / dy] \quad (1)$$

With f = fluid force, η = fluid viscosity coefficient, and the fraction dv/dy refers to the cut velocity, V_c , while the relationship f/A , force per unit of area is called the cutting force, F . Thus, in terms of V_c and F in Equation (1) it could be transformed into:

$$\eta = F/A \quad (2)$$

In this way, both equations (1) and (2) could be taken as expressions that define m and the practical application of these properties will depends on the validity of a series of experimental assumptions, especially when the flow is laminar [7].

3. MATERIALS and METHODS

3.1 Sample Preparation: Canadian bituminous coal was obtained from Texas OilTech Laboratories (Houston, TX), with the bulk of coal crushed by means of an Agata mortar and pestle, to obtain a particle size of 50 to 100 μm .

3.2 Organic Associate Minerals Extraction, OAM:

The extraction of OAM were performed by follows former published procedures and SmCA-S was conducted on a vesel extractor innovation, that allows to monitor thermodynamic experimental conditions [8]. Briefly, both methods employed same mass of grinded coal # 1 and #2 (10 g), which was placed into a glassware and base porcelain fritted thimble with internal diameter of 25 mm and height of 80 mm with the thimble placed inside the extractor's vessel, which is surmounted with a condenser and the vessel suspended above a round bottomed 400 mL flask containing 250 mL of solvent (toluene/hexane, 3:1, Soxhlet). The extractions were performed to proceed under reflux for 24 h (Soxhlet, coal #1) and 4 h for SmCA-S (coal #2 under 100 mL of same mixture of solvents), respectively. After extraction's completion, the solvent was removed in a rotary evaporator system at 45°C and 110 mbar. At least 3 replications for each extraction were performed with the results averaged and the mass of recovered organic material was compared to the initial dried coal/solvent ratio to determine percent recovery as described in equation 3.

$$\%EOM = \frac{EOM_{\text{total(g)}}}{M_{\text{coal(g)}}} \times 100 \quad (3)$$

Where %EOM = percentage of extractable organic matter, EOM_{total} = total organic matter expressed in grams which is the sum of all extracted and identified organic

compounds, M_{coal} = the mass of ground coal sample subjected to extraction.

3.2 Field Emission Scanning Electron Microscopy (FESEM) and EDS determination: Field emission scanning electron microscopy (FESEM) were carried out on a JSM7100F (Jeol Co.) microscope equipped with an Oxford energy dispersive X-ray detector.

For the examination, after powdered samples were mounted on FESEM holder using a carbon tape, the images were taken in various magnifications and analyzed with EDS to investigate quantifiable changes of organic/inorganic components before and after Soxhlet and SmCA-S extraction treatment.

4. RESULTS and DISCUSSION

4.1 FESEM, EDS coal analysis: The Figure 1 shows the FESEM images of crude and treated coals exposed to different magnifications ($\times 500$, $\times 2000$, and $\times 3000$). It is a bit difficult to take clear images in the high magnification mode due to the high resistivity shown by coal samples.

After the two treatment processes, small micrometer size pits were analyzed on which is observed a uniform pattern on the coals surface as depicted by micrographies 1-c and d, respectively.

Especially, the treated coal under SmCA-S method shows clear surfaces and deep porosities not observed on either the crude (Fig 1a-b) and the Soxhlet (1e, 1f), which means SmCA-S can remove large contents of ash (S), alkali and alkaline earth metals (K, Mg) as quantified through EDS analysis. Upon SmCA-S treating, the coal surface shows to be smoother than its counterpart Soxhlet treated sample by comparing micrography's 1c, 1d with 1e, and 1f, respectively. The analysis also shown a relative enhancement of carbon content with substantial decrease of Mg, K, Al, Si, S and other trace metals in the examined grains that suggests the effectiveness of SmCA-S method over the Soxhlet for coal-cleaning in regards of help on reduce of toxic emissions from power plants, an information very helpful in understanding potential health effects of these substances among improvements in thermochemical extraction methods. For the purposes of assessing potential health impacts of trace metal emissions, it is important to know whether these elements are distributed homogeneously throughout a grain of coal sample, or whether their distribution varies on the individual-particle basis. Further investigation of the distribution of trace elements in coal grains with different compositions may lead to the development of better extraction devices tailored for removal of specific trace metals.

Energy dispersive X-ray spectroscopic (EDS) mapping were applied on a crude nanocrystalline coal, which is displayed in Figure 2(a-b). After coal treatment, the EDS shown a prominent peak for carbon, the predominant element in coal #1 and #2 (peak C, Fig 2), respectively.

The same peak is a bit short in the crude sample, instead other prominent peaks are observed in Figure 2A and that correspond to ash (S) and heavy metals (Al, Mg, Si, K) as listed in Table 1.

Table 1. Comparison of EDS chemical components of both crude and after treated bituminous coal (mass %)

Element	Crude	Soxhlet	SmCA-S
C	85.76	75.05	88.0
O	5.98	8.10	5.93
Mg	0.11	0.23	0.07
Al	3.14	4.71	2.26
Si	3.34	8.31	2.37
S	0.77	1.38	0.56
Cl	0.54	---	0.58
K	0.36	1.01	0.24

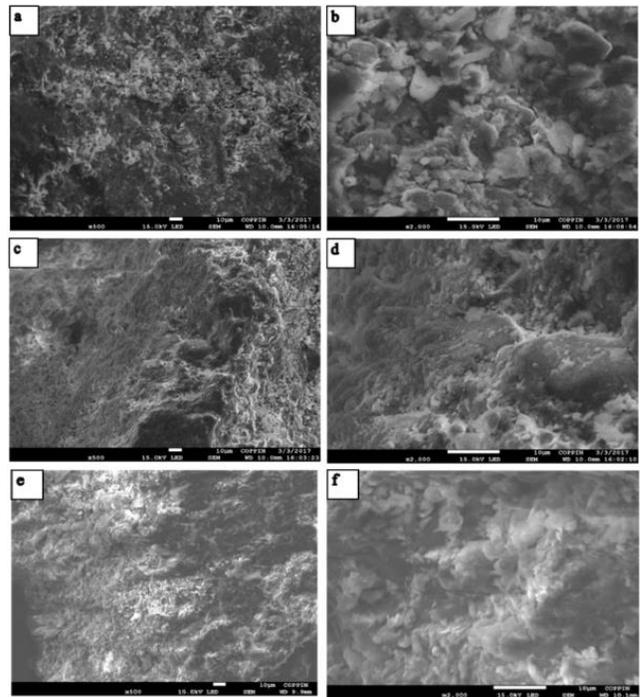


Figure 1. High-resolution FESEM images of crude (a, b); SmCA-S (c, d), and Soxhlet (e, f) treated bituminous coals.

The Figure 2 shows the EDS differences detected on different coal areas of percentages of OAM extracted after SmCA-S (Fig 2c,d) (coal #1) and Soxhlet (Fig 2e,f) (coal #2) respectively. On coal treated with Soxhlet method among irregular shapes observed in its FESEM micrographies (1e, 1f), a large content of organic associated minerals remain on the coal surface although this extraction was performed in continuous reflux for 24 h. In the other hand, the coal treated under SmCA-S thermochemical conditions, the EDS analysis shows an increase on the

carbon content that is evidenced in the flat laminations depicted in the coal smoothy surface (Figures 1c-d).

The organic matter content calculated (OM %) was calculated from the carbon content by multiplying with a value of 1.7 [9]. The derived organic matter content of the coal sample extracted through SmCA-S was substantially higher than the Soxhlet treatment. The filtrate material was recovered in a vial and kept in a dark place at room temperature for several days under gentle evaporation, yielding a deep green oil. Yield, 0.66 g (11.2%) Soxhlet, while 1.04 g (17.7%) were extracted through SmCA-S.

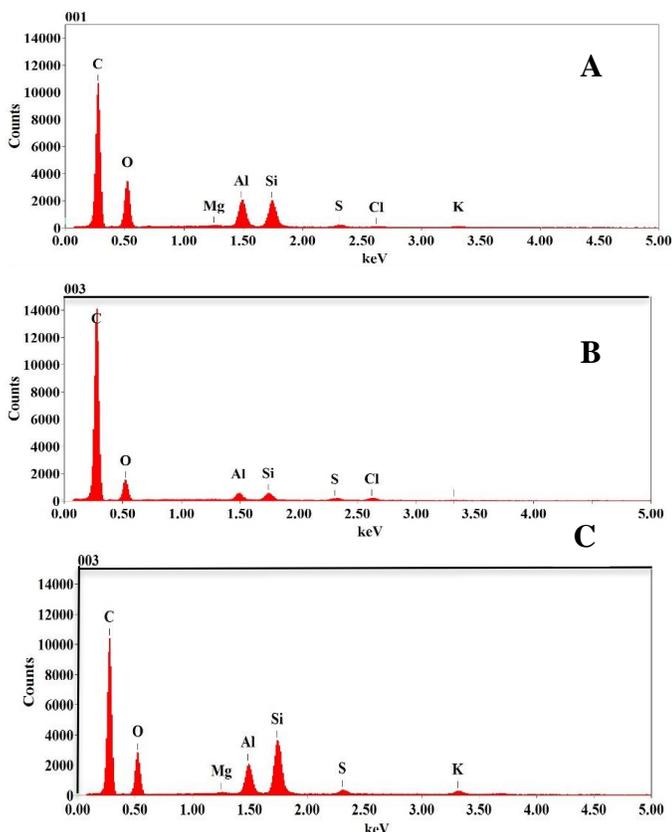


Figure 2. EDS spectra of crude (A); SmCA-S (B) and Soxhlet (C) treated bituminous coals.

CONCLUSIONS

This study has shown the advantages encountered for organically associated minerals extraction by an improved thermochemical technology (SmCA-S) compared with Soxhlet method. The relative enhancement of carbon with substantial decrease of Mg, K Al, Si, S and other trace metals in bituminous coal grains suggests the effectiveness of SmCA-S method for coal- cleaning processes in helping to reduce toxic emissions of organic and inorganic hazards materials. Further investigation of the distribution of trace elements in particles of different compositions will be accompanied for TEM spectroscopy together with GC-MS and TGA polyaromatic ring analysis in a short future.

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