Full Length Article

# Effect of solvent structure and amine addition on the depolymerization of a bituminous Venezuelan coal

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ABSTRACT

This research article describes the solvents composition and structure effects on the depolymerization/extraction yield of a bituminous coal from the Naricual coalfield, located in Eastern Venezuela. Benzene, chloroform, N,N-dimethylformamide (DMF), 3-methylphenol (m-cresol), hexahydropyridine (piperidine) and toluene have been used as solvents; dimethylamine and p-phenylenediamine were used as additives (coal: amine 10:1 ratio), testing possible changes in yield in a Soxhlet extraction system in a 12 h lapse. The extraction/depolymerization capabilities were increased as follow: benzene < toluene < chloroform < DMF < m-cresol < piperidine. Boiling temperature, Hildebrand solubility and empirical polarity parameter $E_T(30)$ do not explain the yield solvent's behavior used in Naricual coals extraction. On the other hand, H-bonding ability and electron-donor availability in the solvent are critical factors in the coal extraction/depolymerization process. These results confirm the important role of specific interactions in determining the extraction/depolymerization behavior of this coal. When amines were added, the yield increased significantly, but in a different extent. Furthermore, added amine opens the coal structure for solvent penetration. Identity of the amine and the synergistic mixture of solvent and an amine are key factors affecting the depolymerization of the coal under study.

## 1. Introduction

In carbochemistry, the coal-derived liquid can be used as precursor for tar, oils, solvents, rubbers, pigments, asphalts, and many other useful products [1]. Several procedures were proven while obtaining liquids from coal: hydrogenation, pyrolysis, liquefaction, controlled oxidation, dry-distillation, solvent-refined coal. Solvent extraction technology has been practiced in the production of clean (low-ash, low-sulfur) coal [2]. During the solvent-assisted depolymerization, the breakdown of different intermolecular forces between coal molecules takes place: H-bonding, π–π interactions, van der Waal's and London forces [3,4]. Depolymerization is the initial path in coal liquefaction [5,6], a treatment that allows to obtain low molecular-weight products. However, for many other solvents, nature of coal-solvent interactions are minimal, limited to the removal of occluded molecules from the macromolecular matrix (extraction).

Bituminous and subbituminous coals reveal low extraction yield

(< 3%) with conventional solvents as chloroform or dichloromethane. On the other hand, several authors have reported higher yields with more aggressive solvents (e.g. pyridine, tetrahydrofuran –THF-, ethylenediamine) [7,8]. Mixture of solvents, pre-demineralization with acids, previous thermal treatment and other added products were also tested [9–13]; in general, solvolysis of coal increases with time and temperature [14]. Low quantities of specific compounds affect the depolymerization extent. Certain aromatic amines added in low proportion in the coal-solvent mixture rise the extraction yield reporting increases from 51.4 to 81.3% [15].

Venezuela has large coal reserves, mainly located in the western region of the country. These low rank coals are from Tertiary age and cover a wide range of chemical and petrographic characteristics [16,17]. Naricual coals are high-bituminous, with potential reserves estimated in 100 MMTM [18]. Only few studies carried out in these coals [19,20] had achieving satisfactory results in terms of growth in extraction yields that resulted from mild to moderate. This article

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**Table 1**
Proximate analysis of parent coal.

| Coals | Proximate analysis | | | | | Petrography | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Moisture (%) | Volatile matter (%) | Fixed carbon (%) | Ash (%) | Calorific value (dmmf)[**] (BTU/lb) | Vitrinite (%) | Liptinite (%) | Inertinite (%) | Ro, % |
| Narical A | 5.51 | 42.80 | 48.39 | 3.30 | | 94 | 4 | 2 | 0.52 |
| Narical M | 3.93 | 40.90 | 50.92 | 4.25 | | 96 | 2 | 2 | 0.60 |
| Narical C | 5.16 | 38.21 | 49.85 | 6.78 | | 95 | 2 | 3 | 0.58 |
| Narical O | 7.01 | 32.88 | 47.89 | 12.22 | | 99 | 0 | 1 | 0.60 |
| Narical S | 4.39 | 38.28 | 53.49 | 3.84 | | 95 | 3 | 2 | 0.60 |
| NCCS | 5.20 | 39.91 | 49.54 | 5.35 | 13800[*] | 96 | 2 | 2 | 0.59 |

* Determined only in the composite.
** Dry, mineral matter free.

studies the use of organic solvents with different extractive efficiency and their relationships with some empirical parameters derived from solvents, as well as the influence of amines on the extraction/depolymerization yields in bituminous Narical coal.

## 2. Experimental procedure

### 2.1. Sample description

A finely crushed Narical Composite Coal Sample (NCCS) was prepared from a mixture of five clean coal seams (dried at room temperature during 72 h before processing: Aragüita, Mallorquín, Capiricual, Orégano River and Santa María) coal sequences from the Narical mines, currently abandoned. The proximate analyses and general petrography results, including % Ro, are summarized in Table 1. The examined coal is classified as high-volatile bituminous B.

### 2.2. Solvents description

Six solvents were examined: benzene, trichloromethane (chloroform), N,N-dimethylformamide (DMF), 3-methyl-phenol (m-cresol), hexahydropyridine (piperidine) and methylbenzene (toluene). The general properties, electron donor- acceptor properties, and solubility parameters of the solvents were obtained from the literature and summarized in Table 2. Some solubility parameters from coal tar pitch "as solvent" from Weinberg and Fen [21] were included in the table for comparative purposes.

A clean and dried coal sample (110 °C under vacuum for at least 6 h) was crushed and sieved through 60 mesh (-250 μm) size sieve. Freshly distilled solvents were used (benzene, toluene, chloroform); and DMF, m-cresol and piperidine without further purification because they had a reagent grade (Aldrich). Two g of crushed coal sample weighted at 0.0001 g were used with a standard Soxhlet extraction assembly at the atmospheric reflux temperatures of the applied solvent. The ratio from solvent to coal was maintained near 100:1 w/w and the extraction time was approximately 12 h. The same procedure was repeated for each sample with the addition of dimethylamine (DMA) and 4-

phenylenediamine (4-PhDA) without further purification (10:1 w/w coal: amine). The liquid product, containing solvent, was vaporized through rotary evaporation (reduced pressure). After this process, the organic residue was further dried in a vacuum oven at 50 °C during ~24 h to remove residual solvent (36 h for the m-cresol extract). All the experiments were performed three times and the average values were reported. Therefore, it is difficult to determine the accuracy of the solvent's retained amount in the extract; extraction yields reported were not "corrected" for possible solvent incorporation. Removal of nitrogen solvents (DMF and piperidine) required washing with a mixed 80% methanol/water solvent, vigorously shaken for thirty minutes and then centrifuged, before vacuum drying.

## 3. Results

The yield (calculated on dry and ash-free basis –d.a.f.-) for coal and the coal/amine extractions (Table 3) are lesser than 4% in benzene, toluene and chloroform. It's obvious that these solvents only removed occluded or weakly bounded organic molecules inside the coal matrix.

Benzene, chloroform and toluene worked like conventional solvents when they react with Narical coal: low yields, an extracted material similar in consistency with a brown semi-solid wax, and strong oil scent. These solvents were classified by Dryden coal-solvent scale [26] as class I, and will only solubilize low-molecular weight organic compounds occluded in the macromolecular coal matrix.

### 3.1. Influence of the boiling point of the solvent

It has been established that the higher the boiling temperature of the solvent is, the higher the extraction yield [26]. There is no connection between the extraction yield and the boiling point. Yield with toluene (0.1%) has no comparison with the yield with piperidine as solvent (50.2% w/w), although both solvents have very similar boiling points. Solvents as DMF or m-cresol, with boiling points higher than piperidine, had lower power extractive.

**Table 2**
Solvent class, polarity and solubility parameters, and electron donor–acceptor number of solvents.

| Solvent | Solvent class [22] | $E_T30$ [23] kcal/mol | Gutmann's parameters [24] | | | Hildebrand solubility parameter [23] | Hansen parameters [25] | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | DN | AN | DN-AN | | Dispersion force | Polar force | Hydrogen bonding |
| Benzene | I | 34.3 | 0.1 | 8.2 | −8.1 | 18.8 | 18.4 | 0 | 2.0 |
| Chloroform | I | 39.1 | 4 | 23.1 | −19.1 | 19.0 | 17.8 | 3.1 | 5.7 |
| DMF | III | 43.2 | 26.6 | 16.0 | +10.6 | 24.8 | 17.4 | 13.7 | 11.3 |
| m-Cresol | IV | 52.4 | – | – | – | 27.2 | 18.0 | 5.1 | 12.9 |
| Piperidine | V | 35.5 | 51 | – | – | 8.7 | 17.6 | 4.5 | 8.9 |
| Toluene | I | 33.9 | 0.1 | 6.8 | −6.7 | 18.1 | 18.0 | 1.4 | 2.0 |
| Coal tar [21] | – | – | – | – | – | ~20–24 [21] | 18.7 | 7.5 | 8.9 |