COAL REFINED SOLUTION, A PRODUCT OF COAL DISSOLUTION IN THE AUTOCLAVE

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ABSTRACT

When speaking of the large coal deposits, comparative to the oil and natural gases ones, it is obvious the fact that the very way these primary energies are used today shall not be mankind, unless, the coal consumption is increased and some new directions are found, viewing a superior capitalization of them by conventional engineering procedures.

This work paper focuses especially on the main solvents that induce degradation of coal intricate structure as well on my researches concerning complex capitalization of coal, i.e. to get coal refined solutions, a raw material in the power industry. Accordingly, an autoclave with a shaking system was employed in which the special coal of the Jiu Valley, Romania, was dissolute in the presence of some hydrogen giving substances and catalysts in different working conditions, reaching thus a dissolution output of about 90% compared to the combustible mass.

It is also emphasized the part played by the hydrogen giving substances in the process of coal dissolution as well the reactions that prevent the birth of some polymers such as semi-coke or coke.

The coal-refined solution was with the help of a chromatograph analyzed and the gravimetric composition was revealed on the basis of I.R. spectra; thus it was concluded that the component C_{14} was predominant (54%).

The properties of this solution are similarly to those of oil, solution from which liquid fuels, such as petrol, Diesel oil, etc. can be obtained through chemical processing.

INTRODUCTION

The complex of substances called coal is made up of an organic mass of C, H, O, N, S and an inorganic mass of mineral substances that are turned into oxides and water by burning.

The chemical structure of coal is quite complex, as X – rays spectra and infrared spectra show, coal is made of condensate polyaromatic macromolecules with unrepeated monomer units (branches, parts), coal is to dissolute into some solvents, more or less depending on the treating conditions (fig. 1).

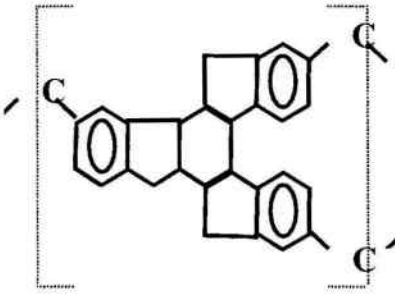


Fig. 1 Pitcoal structure,after H.H. Storch and Morchin

A good solvent that dissolute coal implies certain conditions:

- it should be a good physical solvent for the liquefaction products;
- it should be able to transfer hydrogen;
- it should have hydrogen giving compounds;
- it should have few hydrogen consumers;
- solvent quality index should be > 10.

A good dissolution also implies that the characteristics of the solvent should integrate into an optimum range (Table I).

Table I Optimum Range For The Characteristics Of Solvent Viewing A Good Dissolution.

Characteristics of solvent	Range	Optimum value
Content of hydrogen (%)	8.00 - 9.60	8.80
C / H ratio	0.78 – 0.97	0.87
Aromatic hydrogen (%)	2.75 – 4.3	3.55
Hydrogen in α position (%)	1.60 – 2.25	1.88
Hydrogen in β position (%)	1.60 – 3.55	2.55
Hydrogen in δ position (%)	0.60 – 1.25	0.90

As the literature and the lab dissolution testing say, the solvents have been divided into: non – specific and specific solvents efficient at lower temperatures where the physical processes prevail and reactive solvents of chemical degradation efficient at high temperatures.

The non – specific solvents dissolute a small percentage of coal at a temperature around 100^0 C.

Some of the solvents in this category are organic compounds with low bailing point such as: methanol, propanol, bitanol, acetone, chloroform, ether, carbon tetrachloride, etc. but the solubility of the Jiu Valley special coal is between 4% and 12%.

The coal extract is a wax of vegetal origin that isn't an important part of the coaly substance; it is an extract with no commercial importance.

Among the above – mentioned alcohol's, methanol can work as a hydrogen donor in the presence of a base; the following ionic mechanism is proposed.

$$H-C-OH+O\overline{H}\longrightarrow H-C-\overline{O}+H_2O \qquad (1)$$

$$H-C-\overline{O}+coal\longrightarrow C=O+coal\overline{H} \qquad (2)$$

$$coal\overline{H}+H-C-OH\longrightarrow H-C-\overline{O}+coalH_2 \qquad (3)$$

Thus, the hydrogen given by the donor helps to coal dissolution.

These solvents are also called solvents with a small out put.

The specific solvents can dissolute around 15 – 20%, coaly substances at temperatures of about 200^0 C.

Some of the solvents in this category are the primary aliphatic amines with or without aromatic substitutes or hydroxyls, pyridine and other heterocyclic bases.

According to the results, the primary amines are better solvents than the secundary and tertiary; this mobility decreases as the number of methyl groups connected to the amino group increases.

Generally the nitrogen compunds are better than the oxygen compunds. These properties depend on the nucleophilic properties given by the pair of electrons from the atom of nitrogen or oxygen that turns solvent into a polar fluid.

The results obtained after the dissolution of coals with different contents in carbon show

ever higher dissolution outputs when the content in carbon is lower.

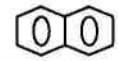
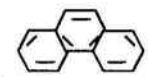
REACTIVE AND DEGRATING SOLVENTS

The degrating solvents extract less coaly substance in comparison with the reactive ones that can extract up to 70% or more, depending on the conditions imposed to the dissolution.

After extraction, the solvents can be almost totally recovered unchanged aut of the solution. Examples of such solvents are: phenantrene and phenantridine. The heavy oil is also recovered from the coal solution in totality.

For the case of the degrating solvents, coal dissolution reaches a maximum at a certain temperature, after which there appears a decreating due to solvent degradation, as a result of polymerization camed aut during extraction (table II).

Table II Dissolution Of The Jiu Valley Special Coal In Degrating Solvents

COAL TYPE	SOLVENT	PERIOD TO BE KEPT AT 400°C (min)	COAL CONVERSION
THE JIU VALLEY SPECIAL COAL	 (naphthalene)	2	18
		4	25
		10	20
		20	15
		30	10
	 (phenantrene)	2	15
		4	20
		10	18
		20	16
		30	14
	$C_{20}H_{42}$ (dodecane)	2	13
		4	21
		10	19
		20	17
		30	16

When using phenantrene for coal dissolution, the free radical of carbon takes hydrogen out of phenantrene, thermically obtain under the form:

Carbon - Carbon ⟶ 2 Carbons$^{\bullet}$ [6]

The radical of phenantrene who takes an atom of hydrogen from another part of the coal fragment gives birth to another radical of carbon. Thus, the phenantrene shall play the part of a hydrogen transfer agent or a hydrogen transferor, otherwise, hydrogen is transferred among parts of coal.

When pressurized hydrogen is added to these solvents, the coal solubility increases due to the fact that the dissolute hydrogen stabilizes the fragments of coal.

The reactive solvents dissolute coal through chemical reactions with it at temperatures around 400^0 C.

The extract differs from a chemical point of view from the ones obtained with degrading solvents. During the process of extraction the solvent is changed essential. The residue plus have extraction the solvent is heavier than the initial coal, which means that a part of the solvent is stuck in the extract.

The reactive solvents interact with coal or with parts of coal, increasing dispersion, volatilization and conversion in soluble products.

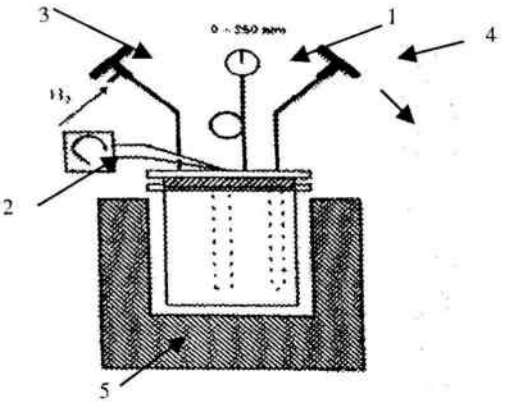
A thermal degradation in soluble fragments and reactions of oxygen transfer occur in this situation. These solvents donate

hydrogen to coal or to coal fragments or act as hydrogen transfer agents.

Tetraline has proved to be the most efficient reactive solvent and that is why all the testing for the dissolution of the Jiu Valley special coal were carried out in the presence of this solvents.

EXPERIMENTAL PARTS

With this end in view, an autoclave without a shaking system was used (fig. 2), where there were introduced 20 g of the Jiu Valley special coal, coking medium oil as a solvent in the absence of the hydrogen giving substance and catalyst, at different maceration periods (table III).



Legend:

1- pressure gauge for recordings of pressure; 2- thermocouple (Fe-const.) for recordings of temperature; 3- tap for hydrogen inlet; 4- tap for gases outlet; 5- electric oven.

Fig. 2 Autoclave for Coal Dissolution

Table III Results of the Jiu Valley Special Coal Dissolution in Autoclave

No.	Coal type	Quantity (g)	Coking medium oil (ml)	Hydrogen giving substance	Catalyst	Temp (^{0} C)	Mace-ration	Dissolution output (%)
1	The Jiu Valley special coal	20	60	-	-	400	1/2	55
2		20	60	-	-	420	1/2	57
3		20	60	-	-	440	1/2	coking
4		20	80	-	-	420	1	59
5		20	80	-	-	420	2	59.2
6		20	80	-	-	420	3	60
7		20	80	-	-	420	1/2	55
8		20	80	-	-	420	1/1	57.6
9		20	80	-	-	420	3	59

According to the centralized data, it can be noticed that the dissolution outputs of the Jiu Valley special coal are low in the absence of a hydrogen giving substance and of the catalyst.

A solid / liquid ratio greater than 1:3 isn't worth as it is inefficient on coal dissolution. The

same thing may be said about the maceration period that should be no more than an hour.

If the coking medium oil is replaced with other solvents: light oil, tar, heavy oil, the dissolution output are < 40%.

With the view to increase the coal dissolution output the dissolution process was repeated in the presence of the said solvents with Tetraline as a hydrogen giving substance (table IV).

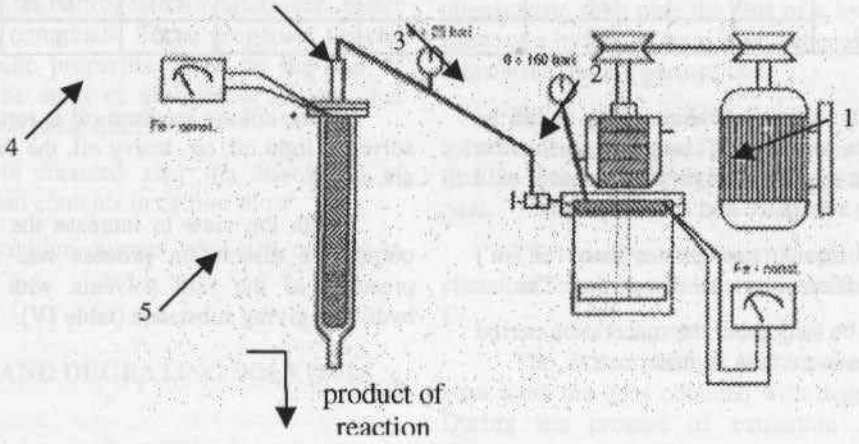
Table IV Dissolution of the Jiu Valley Special Coal in the Presence of Tetraline

No.	Coal type	Quantity (g)	Solvent	Tetraline	Catalyst	Temp. (^{0} C)	Maceration period (h)	Dissolution Output
1	The Jiu Valley special coal	20	Light oil	20	-	400	1/2	47.8
2		20	Heavy oil	20	-	400	1/2	56
3		20	Tar	20	-	400	1/2	59
4		20	Medium oil	20	-	400	1/2	70.23
5		20	Light oil	20	-	420	1/2	48
6		20	Heavy oil	20	-	420	1/2	57.5
7		20	Tar	20	-	420	1/2	61
8		20	Medium oil	20	-	420	1/2	71.5
9		20	Light oil	20	-	440	1/2	semi-coke
10		20	Heavy oil	20	-	440	1/2	semi-coke
11		20	Tar	20	-	440	1/2	semi-coke
12		20	Medium oil	20	-	440	1/2	semi-coke
13		20	Light oil	20	-	420	2	50
14		20	Light oil	20	-	420	3	50.2
15		20	Heavy oil	20	-	420	2	58.2
16		20	Heavy oil	20	-	420	3	58
17		20	Medium oil	20	-	420	2	73
18		20	Medium oil	20	-	420	3	72.5
19		20	Tar	20	-	420	2	62
20		20	Tar	20	-	420	3	62.6

The dissolution output increases with about 10% in the presence of the hydrogen giving substance (Tetraline) and using the coking medium oil as a solvent. Here too, if the maceration period is of 2 and 3 hours respectively, the dissolution output is very less increased.

To draw a conclusion, the optimum liquefaction temperature is of 400-420^0 C and the maceration period is between half and one hour. The coal turning into semi-coke takes place at 440^{0}C due to the process polymerization, as a result of recombination of radicals among them.

Considering that shaking plays an important part in coal dissolution, equipment with an autoclave and a shaking system was designed together with a micro reactor where the catalyst that is to be used is introduced (fig. 3).



Legend:

1- motor ; 2-stirring system ; 3- pressure gauge for recordings of pressure; 4- thermocouple for recordings of temperature (Fe-const.); 5-microreactor with catalyst (MoS_2)

Fig. 3 Laboratory Installation Equipped With A Shaking System

This installation was employed in the dissolution of the Jiu Valley special coal, when using a MoS_2 catalyst (table 5).

TABLE V Dissolution of the Jiu Valley Special Coal in the Presence of MOS_2

No.	Coal type	Quantity (g)	C.M.O. (ml)	Tetraline (ml)	Catalyst (MoS_2)	Temp. (^{0} C)	Maceration Period (h)	Dissolution Output (%)
1	J.V.S.C.	20	20	20	+	400	1/2	82.3
2	J.V.S.C.	20	20	20	+	400	1	83.4
3	J.V.S.C.	20	20	20	+	400	2	83
4	J.V.S.C.	20	20	20	+	400	3	84.2
5	J.V.S.C.	20	20	20	+	420	1/2	84.2
6	J.V.S.C.	20	20	20	+	420	1	84.6
7	J.V.S.C.	20	20	20	+	420	2	85
8	J.V.S.C.	20	20	20	+	420	3	86
9	J.V.S.C.	20	20	20	+	440	1/2	Semi-coke
10	J.V.S.C.	20	20	20	+	440	1	Semi-coke
11	J.V.S.C.	20	20	40	+	400	1/2	84
12	J.V.S.C.	20	20	40	+	400	1	85.2
13	J.V.S.C.	20	20	40	+	400	2	86
14	J.V.S.C.	20	20	40	+	420	1/2	85.2
15	J.V.S.C.	20	20	40	+	420	1	86.3
16	J.V.S.C.	20	20	40	+	420	2	89.8

J.V.S.C. -- the Jiu Valley special coal
+ -- presence of catalyst
C.M.O. – coking medium oil

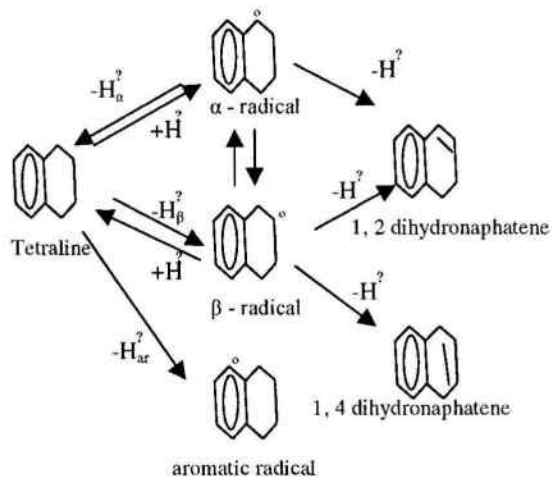
It can be noticed the fact that Tetraline is a very good solvent to turn coal into a refined solution compared to other hydrogen

non-giving substances such as: antracene, naphthalene, phenentrene, etc.

Tetraline may be used as a model of hydrogen giving solvent as it has a simple structure, it is efficient and available to donate hydrogen in certain conditions.

The hydrogen contained by Tetraline is donated to the radicals obtained through coal cracking, giving a rise of the H / C ratio in the obtained products, compared to the initial coal.

The reactions that take place are show as it follows:



carbon — carbon → 2 carbons •

2 carbons • —hydrogen→ coal H

The more the hydrogen giving substance is able to transfer hydrogen, the more the output of coal dissolution is increased.

S.C. PETROBRAZI S.A. analyzed the coal solution and the following composition was found:

Coal solution	Common crude oil
Viscosity	1,32 1,3

Metals		
Ni	40 ppm	25 ppm
Cu	2,5 ppm	2,5 ppm
Fe	75 ppm	65 ppm
Ash	0,06%	0,08%

The following fractions have been obtained through the fractional distillation of the coal solution:

Co-products	C_1-C_2	14%
Fraction 56-175^0 C		12%
Fraction 175-300^0 C		50%

According to the distillation points, liquid fuels of the following types are obtained: petrol, Diesel oil and a fuel oil type residue, fuels also resulted after crude oil distillation.

A chromatographic analysis of the resulting gases shows a high content in H_2 and CH_4.

CONCLUSIONS

- The dissolution of the Jiu Valley special coal depends to a great extend on the existence of a hydro aromatic organic compound called hydrogen giving substance and of a solvent who plays the part of a transit agent of hydrogen from the giving substance to coal, to prevent recombination of radicals that would lead to coke formation.

- A series of physical and chemical factors are involved in the process of coal dissolution such as: petrography compounds, pressure, temperature, catalysts, ratio between solid and liquid, maceration period, etc, factors that contribute to the cracking of the complex structure of coal with the formation of some compounds with a smaller molecular mass.

- A catalyst fell out on an alumina support, reaching a dissolution output of 82-89%, plays a very important part in coal dissolution.

- The characteristics of the product resulted after the coal dissolution is similar to the ones of are product that is turned into fuels such as: petrol, Diesel oil, etc., through the process of distillation.

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