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MASTER'S THESIS

Alternative carbon binders on the basis of petrochemical and coal feedstock 04.04.01 Chemistry 04.04.01.10 Petroleum chemistry and refining

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ABSTRACT

Overall, it is clear from the literature data that in today's world the demand for coal tar pitch and carbon binder like a product in industries is constantly growing (particularly in the aluminum industry). The progressive coal-tar pitch shortage is evidenced. Therefore, it is to base the need to search for new or alternative methodologies and new raw materials for the production of pitch-like a product. The possibility of swelling the coal through different organic solvents to modify its structure was considered. The prospects of obtaining of a pitch from the mixture between coal tar and petroleum as a raw material, at the same time, an idea of the quality of the pitch can be obtained through the analysis of several indicators were demonstrated.

Keywords: PITCH, COAL TAR, ANODE, PYROLYSIS.

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INTRODUCTION

In the last ten years, it has been shown that the production of ferrous and nonheavy metals like steel or aluminum had a constant growth in different countries [1]. Taking account that more than 70% of steel and iron is produced in economical blast furnaces using coal-based coke. In current technology, the production of one ton of metal requires between 500–700 kilograms of expensive blast-furnace coke. Minimizing coke consumption is a high priority today [2]. In the production of blastfurnace coke, a byproduct is coal tar (~4%), which is a valuable source of aromatic compounds [3].

One of the main substances used in different industries to develop different technologies is pitch, which is a viscoelastic polymer that can be natural or manufactured, derived from petroleum, coal tar, or vegetables, different forms of this pitch can also be called tar or bitumen [4]. There are different types of pitch, depending on the way it is obtained or the type of properties it presents, therefore the most popular are: petroleum pitch, bituminous pitch, charcoal pitch, coal tar pitch and synthetic pitch. Pitch is generally prepared by thermal treatment of petroleum/coal derived residues. The properties of pitch are largely dependent on feed properties, thermal treatment temperature, residence time, pressure and additives used. [5]

Therefore, a broad spectrum of important organic compounds may be produced from its distillates. "The pitch is the nonvolatile residue (50% of coal tar) containing a complex mixture of polycyclic aromatic and heterocyclic compounds, is a good source of various carbon materials. Moreover, thanks to its combination of high coking and clinkering properties and its low viscosity when molten, pitch may be used to many process, like producing carbon materials with excellent physico-mechanical properties for the electrode industry, carbon fibers, graphite, semiconductors, construction materials, integrated microcircuits, and also materials for the chemical industry, manufacturing, electrochemistry, nuclear power, and the aerospace industry. Most popular use is as binder in the production of anodes for aluminum electrolysis, in which the pitch plays the main role" [6].

In the actually, the demands for coal tar pitch and requirements for its quality are continuously increasing in various fields, due to the high controls in environmental controls, and the need for it, to be used in processes to obtain by-products particularly in the aluminum industry. Therefore, actions taken at ferrous metallurgy companies for upgrading processes and reducing the consumption of coke lead to a decrease in production of coal tar. Russia's growing deficit is covered by import deliveries, which cannot guarantee a secure future. Moreover, stricter environmental sanctions related to the use of coal tar pitch as a source of cancer-inducing emissions, are supporting the search for alternative raw materials and the development of new pitch binder production techniques.

Alternative methods of producing coal pitch were reviewed in [7, 8]. We know that coking coal contains some quantity of plastic mass, consisting of polycondensed aromatic hydrocarbons. They may be extracted by heating coal in special centrifugal equipment with filtration barriers, but this method requires scarce coking coal with an

elevated content of plastic mass. A promising method of producing a replacement for coal pitch is thermal conversion of coal in solvents, so as to permit more complex extraction of the polyaromatic compounds. Analysis shows that coal's organic mass consists of a crosslinked polymer like structure containing molecules, oligomers, multimers, and other structural fragments (mainly aromatic), which are bound together in various ways [9]. The presence of multiple associative connections of different types gives rise to the crosslinked polymer-like structure of the coal's organic mass and limits its solubility at room temperature and at the boiling point.

The type of association depends on the metamorphic stage of the coal, according to [8]. "In typical coal, association is largely due to molecular interactions, including interactions between π electrons of the aromatic systems and the formation of complexes with charge transfer. In coal of limited metamorphic development, a significant role is played by hydrogen bonds, donor–acceptor interactions, and valence crosslinks (mainly ester and methylene aliphatic bridges). In an effective solvent, solvation of the molecules and fragments of the coal's organic mass disrupts the intermolecular associations. As a result, these groupings acquire some mobility and may enter solution in the solvated state. Such partial dissolution of coal's organic mass is assumed to predominate up to 300–350°C. The ability of the solvent to ensure solvation of the fragments in coal's organic mass and to extract them in solution is often characterized by parameters such as the solubility, the dipole moment, and the donor and acceptor numbers" [9].

1 Theoretical part

1.1 Pitch and its nature

The most technical definition of pitch (Dutch pek, from the Latin pix resin) is the residue from the distillation of tar and tar formed during the thermal processing of solid fuel (coal or lignite, peat, oil shale, wood) or thermolysis of petroleum feedstock (pyrolysis resin) [1]. The main Pitch characteristics are:

- solid or highly viscous black product;
- density 12001300 kg / m3;
- fragile (splits upon impact with a shiny conchay fracture), with a gradual action of the load, plastic, non-conductive;
- insoluble in water, resistant to acids; toxic.

The main components of pitch are polycyclic aromatic and heterocyclic compounds, alkylphenols, organic bases, as well as the products of polymerization and polycondensation of these compounds (groups of substances differing in solubility, asphaltenes, resins, carbenes, carboides). The composition and technological properties of pitch (softening temperature, hardness, wettability, thermal stability, sintering ability, ability to produce coke residue, etc.) significantly depend on the type of raw material and production conditions. We can see an example of how looks pitch as a final product in the figure 1. Depending on the feedstock, pitch is distinguished:

- woody,
- coal,
- petroleum, etc.



Figure1- Pitch as a final product

Thus, the wood pitch (residue from the distillation of wood tar) is a solid (softening point is 81-130C) or plastic (55-80C) product with a high (55-85% by weight) content of polycyclic aromatic hydroxy acids. Of greatest importance in technology is coal tar pitch (a product of coal tar processing), characterized by the

following main quality indicators: softening temperature 67-83 C, ash content no more than 0.4% (pitch grades A and B); softening temperature 135-170C, ash content no more than 0.4% (High-temperature brand).

1.1.1 Uses of pitch

"Pitch was traditionally used to help caulk the seams of wooden sailing vessels, and to coat earthenware vessels for the preservation of wine. Pitch may also be used to waterproof wooden containers and in the making of torches. Petroleum-derived pitch is black in colour, hence the adjectival phrase, "pitch-black". [2]"

"The viscoelastic properties of pitch make it very suitable for polishing high quality optical lenses and mirrors. In use, the pitch forms on an overlay or polishing surface, which is loaded with iron oxide (jewelry blush) or cerium oxide. The surface to be polished is pressed into the pitch and then rubbed against the surface thus formed. Therefore, some pitches have an ability to flow, which can be slowly, regardless of this fact, allowing it to be in constant contact with the optical surface [2]".

1.1.1.2 Uses of coal tar pitch

"Coal tar pitch and binding agents obtained from it are the most important components in the production of various carbon materials. The favorable combination of high coking ability and low viscosity in a molten state is mainly responsible for the high level of the physico-mechanical properties of anode pastes obtained on their basis, electrodes for steel furnaces, low ash pitch coke, fireproof materials, tapping hole mixes, C fibers, coal graphite and construction materials for different purposes, electrical products, and roofing and other C materials, which are used in different branches of industry such as in ferrous and non-ferrous metallurgy, electrode industry, the production of semiconductor materials and integrated micro-circuits, chemical apparatus and machine building, electrochemistry, atomic power engineering, aircraft building, and rocket production.[3]"

"Solid coal tar pitch is extruded into small rods and, for this reason, is often referred to as 'pencil pitch'. In the aluminum industry, coal tar pitch is used as a binder in the manufacture of electrodes which primarily consist of petroleum or anthracite coal. As these electrodes are heated at high temperatures over a period of weeks, the ingredients in the electrodes are converted to C. For this reason, coal tar pitch is also often referred to as 'C pitch' or 'binder pitch'. Additional synonyms for coal tar pitch include 'roofing pitch' because of its use in the roofing industry and 'target pitch' because of its use in the manufacture of clay targets. [4]"

Coal-tar pitch is used in the manufacture of graphite electrodes for steel arc furnaces. It is also used to impregnate and strengthen refractory brick (for lining industrial furnaces), and in surface coatings, such as pipe-coating enamels and black varnishes used as protective coatings for industrial steelwork and as antifouling paints for boats. It is also used as a component in the manufacture of activated C, C refractory for blast furnace lining and tap-hole clays. Hard pitch is used as a binder for foundry

cores. It is also used to produce pitch coke, which is used as the C component of electrodes, carbon brushes, and carbon and graphite articles.

Coal tar pitch is an industrial product which is typically dispatched in bulk to customers as either a liquid or a solid. It is often supplied to customers via rail in either tanker car (liquid pitch) or hopper cars (solid pitch).

1.2 Pitch production and main technologies

The pitch is commonly produced from coal tar by product of high temperature coking coal in the manufacture of metallurgical coke, process in which that liquid yield represents less than 4 %. The tar predominantly contains a mixture of bicondensed and polycondensed aromatic hydrocarbons (PAHs) and also compounds with heteroatoms in rings (predominantly nitrogen bases from the quinoline and acridine series, 1-2%) and phenols (1-2%)" [2]. "Upon distillation, 8-12% of a naphthalene fraction, 5-9% of an absorption fraction, and 21-26% of an anthracene fraction, which boiled away to 360° C, were separated. The residual part of the tar (pitch) contained nonvolatile and low volatile sub stances, whose average yield was about 2% on a coking charge basis.

"At room temperature, pitch appears as a uniform solid, which mainly consists of a mixture of PAHs with four or more aromatic rings. An important qualitative characteristic of pitch is its group composition evaluated based on solubility in different organic solvents: the concentrations of substances soluble in petroleum ether (γ fraction), soluble in toluene but insoluble in petroleum ether (β fraction), and insoluble in toluene (α fraction)" [5]. "In turn, the α fraction is subdivided into the fractions soluble in quinoline (α 2 fraction) and insoluble in quinoline (α 1 fraction). The group composition is primarily responsible for the techno logical properties of pitch as such softening temperature, dynamic viscosity, fluidity at a specific temperature, coking property and the yield of coke residue. [6]"

With a common similarity of requirements imposed on pitches and the binding agents of coke– pitch compositions for different purposes, there are specific differences. Table 1 summarizes the requirements imposed on the quality of pitches in the aluminum industry, where they are mainly used as a binding agent for the preparation of anode paste and burned anodes. For achieving standard quality indices, additional methods are used for the heat treatment of pitch: thermosetting at elevated temperatures ($400-430^{\circ}$ C), oxidation under controlled conditions at a temperature of $300-350^{\circ}$ C, or vacuum distillation.

Table1- Characteristics of the properties	of coal tar	pitches u	used un th	he product	ion of
aluminum (GOST 10200)					

Quality index	Testing method		Standa	ard for gra	de
	-	А	В	B1	V
Softening temperature, °C	GOST 9950, item 4.3	65–70	67–73	72–76	85–90
α fraction, wt %	GOST 7847	24–28	25–31	26–31	≥31

		Standard for grade					
Quality index	Testing method						
		Α	В	B1	V		
α 1 fraction, wt %, no higher than	GOST 10200, item 4.4	6.5–7.2	8.0	10	12		
Yield of volatile substances, wt %, no higher than	GOST 9951	59–63	58–62	59	53–57		
Ash content, wt %, no higher than	GOST 7846	0.3	0.3	0.3	0.3		
Coke residue, wt %, no lower than	ISO 6998	_	-	52	55		
Water content, wt %, no higher than	GOST 2477, item 4.5 GOST 10200	4.0	4.0	4.0	4.0		

These methods are intended for increasing the con centration of a specific type of high boiling fractions, which improve the coke forming, rheological, and other properties of a pitch binding agent. The type and structure of the resulting high boiling compounds are determined by the utilized treatment method. Thus, the prolonged thermosetting at a high temperature of 400–430°C facilitates the occurrence of dehydrogenation and condensation reactions with the formation of low volatile polycondensed aromatic molecules. Upon the vacuum distillation and thermal oxidation, low volatile substances are formed due to crosslinks of the biphenyl type, which prevent the formation of undesirable ordered mesophase structures.



Figure 2 - Schematic diagram of a mesophase particle in pitch [6]: (1) isotropic phase, (2) mesophase particle fragment, (3) amorphous phase, and (4) crystallites.

The microstructure and the presence of mesophase microspheres of a specific size are also the important characteristics of pitches and binding agents in the production of graphitized electrodes [1, 5]. Mesophase formations in a pitch binding agent are considered [6, 7] as hematic liquid crystals, which consist of flat polycondensed aromatic molecules packed in bundles in parallel to each other. According to published data [6, 7], their nucleation comes into play on the heating of

pitch of a specific composition at a temperature of about 350°C as a result of the secondary supramolecular ordering of the crystal nuclei formed showed in the Figure 2. "On heating to 460–470°C, bulk crosslinking leads to the hardening of a mesophase with the formation of semi coke with the structure responsible for its capability for graphitization at a high temperature [4] considered mesophase pitches and microspheres separated from them as promising fillers for the production of single component fine grained carbon materials with increased uniformity and physic mechanical characteristics maximally possible for artificial graphites".

Therefore, "the needs for coal tar pitch continuously increase in different branches of industry. The main user is the aluminum industry. The domestic by product coking industry cannot currently ensure half of its needs for pitch. The deficiency is made up by imports from Ukraine, China, and Kazakhstan. However, the growing need for pitch in China because of the intensely developing aluminum industry leads to the gradual reduction of imports and an increase in the cost. The import of pitch from the Ukraine also does not have reliable prospects because Ukrainian producers attempt themselves to diversify export into the EEC countries and the United States, and this can lead to the discontinuance of deliveries into Russia [13]."

"The planned increase in the production of aluminum will lead to an even larger negative balance on pitch. At the same time, measures for the modernization of ferrous metallurgy processes directed toward decreasing the consumption of metallurgical coke already led to a decrease in the production of coal tar in recent years" [8, 9]. An increase in the number of blast furnaces with the injection of powdered coal into the furnace and the largescale development of a competing arc furnace steelmaking process will lead to a further decrease in the need for coke and, hence, to a decrease in the production of coal tar pitch.

In the aluminum business with the use of coal tar pitch, there is an additional risk factor related to environmentally hazardous production because of the formation of a large number of harmful PAHs, including benzo(a)pyrene" [10, 11]. The Soderberg technology, which is used for the production of 68% aluminum in Russia, is characterized by an increased environmental hazard. In some countries, at ecologists' insistence, electrode pitch specifications include the concentrations of these pollutants. The production of alternative pitch abroad is based on the use of crude oil materials.

"Petroleum pitch has more favorable environmental characteristics because of the considerably smaller concentrations of carcinogenic PAHs. In 1991, specialists from the Institute of Petroleum Refining and Petrochemistry, Bashkortostan, Russia implemented a technology for the production of petroleum pitch on a pilot scale [12]". "However, an increased sulfur content and a lowered coking ability led to unsatisfactory mechanical and physical properties and the high consumption of anodes formed on its basis. At present, the industrial production of petroleum pitch is absent from Russia. The combination of petroleum and coal raw materials makes it possible to increase the quality of binding agents [2]". "On an industrial scale, petroleum–coal pitches are produced by Koppers Inc. (the United States) and Ruetgers (Belgium) [13, 14]". They are used for the manufacture of both burned and self-fired anodes [15]. "In the course of the commercial tests of hybrid pitches containing 40% petroleum and 60% coal raw materials at the Elkem Lista and Alcan aluminum production units, which use the Soderberg technology, the emissions of PAHs and benzo(a)pyrene were decreased by 50–60% [16]". "The studies of Russian authors [17–20] on the development of domestic technologies for the production of hybrid pitch were based on the use of raw coal together with the low sulfur petroleum pyrolysis fractions and the tar fractions of the pyrolysis of shale". "In these studies, an important task was to examine the conversion of pitch raw material in the course of its interaction with different fillers in pitch–coal compositions [20]."

A substitute for coal tar pitch (in order to expand the raw material base and due to the lower content of carcinogenic components) can be a pitch of petroleum origin. It is of the following types:

- binders for obtaining electrodes and graphite products;
- impregnating dispersed materials;
- briquettes for coal, coke;
- fiber-forming;
- special;
- raw materials for coking.

The final stage of the process is evacuation of the final product to remove low molecular weight substances and gaseous components. The main types of raw materials for thermolysis units: pyrolysis resins with a high content of aromatic compounds and low-sulfur distillate cracking residues (to obtain electrode binders and impregnating pitch); non-scarce oil residues asphaltites of deasphalting, cracking residues of visbreaking of tar and other products (for obtaining briquette binders, including oil sintering additives).

Resins for pyrolysis of gases, gasoline or gas oil are considered suitable raw materials for the production of pitch. Pyrolysis resin contains polycyclic aromatic hydrocarbons (up to 60%) and unsaturated compounds prone to polymerization reactions at relatively low temperatures with the formation of gaseous products.

The temperature of thermolysis of the raw material is 360- 420C, the pressure is 0.10.5 MPa, the duration of the process is up to 10 h. The yield of petroleum pitch from tar is about 30- 35% by weight; by-products of the process gases, gasoline and gas oil fractions.

Solid pitches derived from petroleum and coal tar are widely used sources for roofing materials, protective surface coatings and binders for aluminum-smelting electrodes [21]. Moreover, mesophase pitch is an important potential feedstock for high-value industrial carbon materials such as carbon fibers, graphite and electrodes [22,23]. The difficulty of high quality and tailored production of carbon materials arises from the incomplete understanding of the underlying reaction mechanisms during processing which is hindered by the insufficient compositional and structural knowledge of the raw pitches, the critical intermediates and the final products.

Thus, characterization methods to structurally analyze the molecular components of solid pitch with regard to their elemental formula, their potential size, shape, and degree of saturation as well as the presence, length and positions of alkyl chains are strongly desired.

1.2.1 Coal tar pitch

Coal tar-pitch is a thick, black, viscid liquid formed during the distillation of coal, that upon further distillation yields compounds, as benzene, anthracene, and phenol, from which are derived a large number of dyes, drugs, and other synthetic compounds, and that yields a final residuum (coal-tar pitch) which is used chiefly in making pavements.

Coal tar pitch is a byproduct of turning coal into coke or coal gas. It is a sticky, dark brown or black liquid that resists flowing and has a very strong smell. The actual components that make up coal tar pitch vary because the chemicals in the coal it comes from differ [24]. Even so, it coals tar pitch is primarily made up of a wide variety of different phenols and polycyclic aromatic hydrocarbons. While coal tar does have medicinal uses in treating some skin conditions, it is primarily burned as a low-cost fuel or further processed into other materials.

While there may be hundreds of different chemicals in coal tar pitch, phenols and polycyclic aromatic hydrocarbons make up two large classes of chemicals. Phenols are a complex classification of molecules that are typically very caustic and often harmful even in small quantities. Polycyclic aromatic hydrocarbons are dichotomous substances that are both extremely harmful to life and believed to be necessary for life to exist at all [25]. They are present in nearly all air and food to some degree, although the concentration in coal tar pitch is much higher.

Coal Tar Pitch has been traditionally used for manufacturing Carbon Anodes and Electrodes for Aluminum and Graphite Industry. The biggest companies in the manufacturing of Coal Tar Pitch are strictly controlled for a good quality High Temperature Coal Tar by Latest Vacuum Flash Distillation Process as we can see in figure 3.

Therefore, they are monitoring and controlling all the necessary Physical and Chemical properties that are important for the performance of Pitch. These properties include:

- Softening Point
- Density and Viscosity
- Coking value
- Toluene Insoluble
- Beta-Resin
- Quinine Insoluble
- Sulphur and Metals
- Ash



Figure 3 - Coal tar pitch used as a binder

1.2.1.1 Properties

The aromatic hydrocarbons in coal tar pitch include: acenaphthene, fluorene, 2phenanthrene, 1-methylfluorene, methylfluorene, anthracene, cyclopenta[def]phenanthrene, fluoranthene, acephenanthrylene, pyrene, benzo(a)fluorene, benzo(b)fluorene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo[e]pyrene, benzo(a)pyrene, perylene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene, and anthantrene. Tar bases/N2 containing heterocycles in coal tar pitch include acridine, and carbazole. The sulphur (S) containing heterocycles in coal tar pitch include dibenzothiophene [26]. The O2 containing heterocycles/furans in coal tar pitch includes dibenzofuran.

At room temperature, pitch appears as a uniform solid, which mainly consists of a mixture of PAHs with four or more aromatic rings. An important qualitative characteristic of pitch is its group composition evaluated based on solubility in different organic solvents namely (i) the concentrations of substances soluble in petroleum ether (gamma fraction), soluble in toluene but insoluble in petroleum ether (beta fraction), and insoluble in toluene (alpha fraction). In turn, the alpha fraction is subdivided into the fractions soluble in quinoline (alpha-2 fraction) and insoluble in quinoline (alpha-1 fraction). The group composition is primarily responsible for the technological properties of pitch such as softening temperature, dynamic viscosity, fluidity at a specific temperature, coking property, and the yield of coke residue.

Coal tar pitch is non-explosive and non-oxidizing in nature. It has affinity and binding capacities to other carbon products (e.g. petroleum coke). The typical physical-chemical characteristics of coal tar pitch are presented in Table 2.

Property	Value	Comment/ Reference
Physical state (at ambient temperature)	Black solid	
Melting point [°C]	65 - 150 °C	softening range; CCSG 2006*
Boiling point [°C]	>360 °C	at 1013 hPa
Density [g/m ³]	1.15 – 1.40	at 20 °C; ASTM D 71; CCSG 2006*
Vapour pressure [hPa]	< 0.1	at 20 °C;
Water solubility [mg/L]	~0.040	16 EPA PAHs, at a loading of 10 g/L at 22 oC; RÜTGERS VFT 1999
Partition coefficient n octanol/water (log value)		not applicable
Flash point [°C]	>250	ISO 2719; CCSG 2006*
Autoflammability [°C]	>450	ignition point at 1013 hPa; DIN 51794 ; CCSG 2006*
Explosive properties	not explosive	CCSG 2006*
Oxidizing properties	not oxidizing	CCSG 2006*

Table 2 - Physic-chemical characteristics of coal tar pitch

*CCSG 2006: Internal communication, Coal Chemicals Sector Group/CEFIC 2006

The water solubility value was determinate through the scope of a comprehensive analytical program on the availability of polycyclic aromatic hydrocarbons (PAH) from pitch in water (RÜTGERS VFT 1999), a column containing 10 g of finely powdered pitch (20 - 200 μ m) was force-perculated by 1.1 L of tap water (water recycling for 1 week)". "Each experimental period was terminated by withdrawal of 1 L of the extract and renewal of the volume by freshwater exchange of 1 l each. After the first run, 36.5 μ g PAH/L were found; after 15 cycles, the PAH decreased to 11.8 μ g/L, and after 39 cycles to 0.9 μ g/L. The first water-soluble fraction was dominated by the presence of acenaphthene, phenanthrene, fluoranthene, and pyrene, followed by naphthalene and fluorene. All other PAHs were distinctly below 1 μ g/L. The total cumulative amount of water-extractable EPA PAHs amounted to approx. 370 μ g/10g (= ~0.004 %).

1.2.1.2 Production

Coal tar pitch is commonly produced through the thermal process coking of coal in the manufacture of metallurgical coke is a byproduct. The tar predominantly contains a mixture of bi- condensed and poly-condensed aromatic hydrocarbons and also compounds with heteroatoms in rings predominantly nitrogen bases from the quinoline and acridine series, 1 % to 2 % and phenols (1 % to 2 %). Upon distillation, 12 % of a naphthalene fraction, 5 % to 9 % of an absorption fraction, and 21 % to 26 % of an anthracene fraction, which boiled away to 360 deg C, are separated. The residual part of the tar is the pitch which contains nonvolatile and low volatile substances, whose average yield is around 2 % of the coking coal charge used for high temperature carbonizing.

The industrial production of coal tar pitch consists of the fractional distillation of the coal tar at a temperature around 400 deg C showed in the figure 2. By this method, the coal tar yields a series of liquid fractions suitable for different industrial applications and a residue which is solid at room temperature, called coal-tar pitch. Two different types of coal tar pitches are usually produced namely (i) binder grade, and (ii) impregnating grade [27]. The main difference between these pitches resides in the quinoline insoluble content (much lower in the impregnating grade coal tar pitch) and in the softening point (around 110 deg C, for binder grade and around 90 deg C, for impregnating grade).

The heaviest coal tar distillation fraction, which distils between around 270 deg C to 400 deg C, is anthracene oil. This fraction, composed of 3 to 5 ring aromatic ring polycyclic aromatic compounds (PACs), has eluded all attempts at polymerization by conventional thermal treatments at atmospheric pressure. Its transformation into a pitch requires the use of specialized forms of treatment that allow the polymerization of low-molecular weight PACs to take place. Some companies have developed an industrial process to transform crude Coal Tar into pitches. This process involves thermal oxidative condensation and subsequent thermal treatment and distillation until the pitch reaches the desired softening point showed in the figure 4.

This type of pitch is produced with the specific aim of fulfilling the requirements for binder and impregnations grades, mainly for carbon (C) anodes and graphite electrodes. For this reason, their use in other fields, such as precursors for advanced C materials, normally requires a pre-treatment of the commercial pitches in order to adapt their composition and characteristics for their further utilization.

For example, thermal treatment in an inert atmosphere and air-blowing are the processes generally used to reduce the emission of volatiles during pitch processing and also to increase pitch C value, without altering most of the fundamental characteristics of the pitch (e.g., wetting capacity, fluidity, etc.). Basically, thermal treatment can be considered as an interrupted carbonization (350 deg C – 450 deg C) which involves distillation, polymerization and even the formation of mesophase. The result is pitch which is able to generate carbons with a lower porosity, higher density and pre-graphitic order. All these improvements make thermally treated excellent precursors for matrices of different types of composites, C fibres, self-sintering graphites, etc [28]. On the other hand, air-blowing has similar effects to thermal treatment but at lower temperatures (less than 350 deg C). This is since oxygen (O_2) promotes the formation of free radicals which favour polymerization reactions. In this case, polymerization occurs via the formation of planar macromolecules and the formation of cross-linked structures. The latter prevents mesophase development during air-blowing.



Schematics of the production of coal-tar pitch and anthracene oil-based pitch

Figure 4 - Schematics of the production of coal-tar pitch and anthracene oilbased pitch

The coal tar pitch contains a large number of substances. It is solid at room temperature and consists of a complex mixture of numerous polycyclic aromatic hydrocarbons (PAHs), their methyl and polymethyl derivatives, and heterocyclics, and shows a broad softening range instead of a defined melting temperature. The hydrogen (H₂) aromaticity of coal tar pitch (ratio of aromatic to total content of H₂ atoms) varies from 0.7 to 0.9.

The coal is heated to a temperature of approximately 1100°C in a coke oven to produce coke (the primary product) and by-products such as, coke oven gas, coal tar light oil, and coal tar [16]. Typical yields are 70% solid products and 30% liquid products. The yield of coal tar, the feedstock for producing coal tar pitch, from a ton of coal is 30--45 liters (8-12 gallons). This pitch has many uses, but the main use of the pitch produced is used as a binder for petroleum coke to produce anodes and graphite electrodes for the aluminum industry. Figure 5 shows the flow scheme from coal coking to coal tar pitch production [29]. As the flow scheme indicates coal tar pitch is produced by the distillation of coal tar.



Figure 5 - Coal Coking to Coal Tar Pitch

1.2.2 Petroleum pitch

Petroleum pitch is an alternative and supplement to coal tar pitch. The PAH level is up to 10 times lower then coal tar pitch without considerable lowering of the carbon content. Petroleum pitch is used for the production of refractory bricks, clay pigeons and as an impregnation pitch for graphite electrodes. It is also used as a blend into coal tar pitch and for other specialty applications.

Many petroleum products are referred to as "pitch" by the petroleum industry. This fact has the potential to cause considerable confusion outside the refining community. In most cases, the different types of petroleum pitch share only the commonality of being black solids at room temperature. The individual characteristics of petroleum pitches vary as functions of feedstock and the specific processes used in their manufacture. Feedstocks can range from a predominantly aliphatic to predominantly aromatic type chemical structure. A reaction step is used to generate and/or concentrate the large molecules typically observed in petroleum pitch [30]. The most common processes used to generate petroleum pitches are singularly or a combination of (a) solvent deasphalting, (b) oxidation, and (c) thermal processes. Solvent deasphalting is used to separate fractions of various heavy oils.

Solvent deasphalting involves mixing the feedstock with a paraffinic solvent such as propane, butane, or pentane. The mixing of the feedstock with these light paraffinic solvents causes precipitation of the molecules with higher molecular weights and aromaticities. The chemical and physical properties of this type of petroleum pitch are more closely associated with asphalt cements used for road paving. Typical properties include a specific gravity of approximately 1.0 glee at 60 F, with the chemical composition containing significant amounts of nonaromatic hydrocarbons and high levels of iron, nickel, and vanadium. Various grades of pitch can be produced by the oxidation of heavy petroleum hydrocarbons. Although oxygen is used in the process, the products typically do not contain significant amounts of oxygen. During this reaction, the presence of oxygen is successful in generating free radicals that induce polymerization reactions. The chemical properties of these products will depend upon the starting material and degree of reaction, but the pitches produced typically have low coking values and high viscosities. Thermal processing .is. used to produce petroleum pitch as noted in several patents. Thermal processing has traditionally been used to produce the high specific gravity and aromaticity petroleum pitches referred to in the introduction. The thermal processes typically employ heat treatment temperatures in the range from 300 to 480"C. A typical flow scheme for producing petroleum pitch from crude oil by thermal processing is given in Figure 6.



Figure 6 - Crude Oil to Petroleum Pitch

Marathon Ashland Petroleum LLC uses a proprietary method for petroleum pitch production. The method produces a highly aromatic petroleum pitch containing few solids and a viscosity comparable with coal tar pitch.

1.2.3 Developing Coal Tar/Petroleum Pitches

In the late 1980's/early 1990's Koppers Industries adopted the development of coal tar/petroleum pitches as one of its strategies for dealing with the developing coal tar supply deficit. One of the leading concepts of the product development effort was that successful coal tar/petroleum pitch products employ coal tar and petroleum components whose properties are compatible. Furthermore, the composition and properties of the individual pitch components must be controlled to ensure final

product quality [31]. The first task of the product development effort was identification of an acceptable petroleum component for producing a superior coal tar/petroleum pitch. Approximately 100 petroleum materials have been evaluated during this program with the most favorable material identified being petroleum pitch produced by Marathon Ashland Petroleum Company.

The next task of the product development effort was identification of acceptable methods of combining the coal tar and petroleum components into the final binder pitch product. It was discovered that special care must be taken to obtain homogeneous product and appropriate processes were developed.

A very positive aspect identified during the development of coal tar/petroleum pitches is the opportunity to build on the positive characteristics of both the coal tar and petroleum components to produce a quality product with equal or improved properties. For example, the low sulfur content of coal tar pitch offsets the higher sulfur content of petroleum pitch and the low metals content of petroleum pitch offsets the higher metals content of coal tar pitches.

The product development effort took a dual product path with one product targeted for prebaked anode and graphite electrode binder applications. This product eventually contained approximately 15 % of the petroleum component and 85 % of the coal tar component. It was designed to perform in a similar fashion to the traditional coal tar binder pitch. The product has been designated Type A pitch. Typical properties of Type A pitch are given in Table 3. The second product was developed specifically to reduce polynuclear aromatic (PNA) emissions from Soderberg plants. This product has been designated Type B pitch. Type B pitch is produced by a patented process x which results in a binder pitch which contains 40 % less PNA's than a typical coal tar pitch. Type B pitch is composed of approximately 40 % of the petroleum component and 60 % of the coal tar component. Typical properties of Type B pitch are given in Table 3. A discussion of the development history of these two products follows. After the final composition of Type A pitch was set, the next step was bench scale evaluation of the binding characteristics of the product with the production of laboratory anodes [32]. Two separate bench scale evaluations were conducted. The first evaluation used pitch produced in the laboratory, while the second evaluation used pitch from a 200-ton batch of Type A pitch produced commercially. These bench scale evaluations gave very positive, so plans were made to conduct commercial trials of Type A pitch. The first commercial trial of Type A pitch was a fourteen-month trial conducted at a large smelter. During the trial 16,700 tons of Type A pitch were used to produce 115,250 vibroformed anodes weighing 908 kg each.

The conclusions of the trial were that there were no significant differences between anode quality or performance when Type A pitch was used as the binder. A number of additional commercial trials indicated that Type A pitch was an acceptable product. Type A pitch is now a proven commercial product with about five years of commercial use. The product development path of Type B pitch was similar to that of Type A pitch. After development of the final composition, bench scale evaluation of the binding characteristics of the product was performed with the production of laboratory anodes. Again, the bench scale evaluation gave very positive results, so plans were made to conduct commercial trials of Type B pitch. Unlike Type A pitch, Type B pitch has been evaluated commercially in both prebaked and Soderberg applications. The pre baked trail consisted of 520 tons of Type B pitch being used to produce 2,100 anodes weighing 825 kg each. The anode forming conditions were not adjusted for Type B pitch use and the trial anodes caused no significant problems with pot operation. However, average anode density and carbon consumption were slightly inferior for the Type B anodes. The Soderberg trail of Type B pitch consisted of the used of 1,000 tons of Type B pitch in a commercial Soderberg plant [30,32]. The trail Soderberg anodes performed well, and a significant reduction in PNA emissions was realized. Presently Type B pitch does not have the extent of commercial use as Type A pitch.

Property	Coal Tar Pitch	Type A pitch	Type B Pitch	Petroleum Pitch
Softening Point, °C	109.4	108.5	112.9	108.7
Toluene Insolubles,	27.5	25.8	29.6	3.5
wt. %				
Quinoline	13.1	12.6	13.9	0
Insolubles, wt%				
Beta Resins, wt. %	14.4	13.2	15.7	3.5
Coking Value, wt. %	57.8	56.3	58.4	47.1
Ash, wt.%	0.17	0.14	0.11	0.03
Specific Gravity	1.336	1.32	1.31	1.225
Sulfur, wt. %	0.64	0.68	0.78	1.30

 Table 3 - Properties of Typical Pitches

As previously discussed, a second driver for the development of coal tar/petroleum pitches may be environmental regulations. Type B pitch was specifically developed to address this issue. Due to the lower processing temperature used to produce petroleum pitch the severity of thermal cracking achieved is much less. The reduced thermal cracking results in a product with a significantly lower PNA content. The benzo(a)pyrene (B(a)P) equivalent of coal tar is 24,930 ppm and Type B pitches is 15,000 ppm.

With the likelihood of increasing environmental pressures for the reduction of PNA emissions, Type B pitch may be the most economical alternative to achieve significant PNA reductions.

1.2.4 Health Information

The American Conference of Governmental Industrial Hygienists (ACGIH) and the Occupational Safety and Health Administration (OSHA) have each established a permissible 8-hour time-weighted-average (TWA) exposure level of 0.2 mg/m3 for the volatiles that are emitted from coal tar pitch ("coal tar pitch volatiles"). This number represents the average airborne exposure in any 8-hour work shift of a 40hour work week which shall not be exceeded. According to OSHA, it is also the highest level of exposure an employee may be exposed to without incurring the risk of adverse health effects. OSHA considers engineering controls, such as ventilation and automation, the best method for controlling exposure to coal tar pitch volatiles. Respiratory protection to limit inhalation exposure and protective clothing to prevent dermal exposure to coal tar pitch and coal tar pitch volatiles are also recommended, although maintaining exposures below the TWA level is preferable.

Acute, or short-term, exposure to coal tar pitch has been associated with several health effects. For instance, coal tar pitch is a phototoxic substance. This means that dermal contact with coal tar pitch in the presence of ultraviolet light (sunlight) can result in a skin reaction similar to an exaggerated sunburn, as well as blisters. Short-term exposure in the absence of sunlight may also irritate the skin and cause other skin conditions such as dermatitis and acne [34].

Additional health effects associated with short-term exposure to coal tar pitch include eye and respiratory tract irritation; severe burns from exposure to hot liquid coal tar pitch; and respiratory difficulty, convulsions, and possible cardiovascular collapse from exposure to airborne concentrations of coal tar pitch mist or vapor significantly beyond the 8-hour TWA workplace exposure limit of 0.2 mg/m3. Several agencies, including the International Agency for Research on Cancer (IARC), the National Toxicology Program (NTP) and the ACGIH, have evaluated coal tar pitch with respect to its carcinogenicity and concluded that it is a human carcinogen. Other agencies, such as the National Institute for Occupational Safety and Health (NIOSH) and the Agency for Toxic Substances and Disease Registry (ATSDR) have also evaluated the potential health effects associated with coal tar pitch. These evaluations, particularly those from the NTP, NIOSH and ATSDR, are not limited to coal tar pitch, but rather include assessments of health effects associated with other products derived from coal, including soot, coal tar and creosote, as well as other industries from which coal tar is derived, including gas works and coke ovens.

It is important to distinguish between the potential hazards posed by exposure to coal tar pitch and those posed by exposure to different derivatives of coal. When the available scientific and medical literature is limited to coal tar pitch, chronic (or long-term) exposure to coal tar pitch above the 8-hour TWA workplace exposure limit of 0.2 mg/m3 and in the absence of proper personal protective equipment has been associated with cancers of the skin, lung and bladder. The risk of lung and bladder cancer has largely been associated with studies of aluminum industry workers employed for many years in a particular industrial process that continuously bakes coal tar pitch 24 hours a day at temperatures in excess of approximately 900 to 950 degrees Celsius. Similar exposures are not expected among the general population. The risk of skin cancer has largely been associated with historical studies and anecdotal reports of workers who did not follow good personal hygiene practices. In particular, the studies and reports suggest that exposed workers did not regularly bathe or wash contaminated clothing. Similar exposures are not expected among workers today who follow good personal hygiene practices and wear proper personal protective equipment [35]. Much of the data relating to skin cancer also derives from animal studies using dermal administration.

There is no evidence in the published literature that low level or incidental exposure to coal tar pitch causes skin cancer in animals, but continuous dermal exposure for long periods of time has been shown to cause skin cancer in mice. There

are no long-term ingestion studies or inhalation studies with coal tar pitch. There is no evidence in the scientific literature that low level or intermittent exposure to coal tar pitch causes any type of cancer in humans. There is also no evidence in the scientific literature that low levels of coal tar pitch in soils, sediments, groundwater, surface water, or drinking water cause cancer in humans exposed to these media. Besides cancer, long-term exposure in the absence of good personal hygiene practices can also affect skin pigmentation and may cause skin growths. Additional data also suggests that coal tar pitch is both a mutagen and a reproductive hazard, which means that longterm exposure to the substance may cause genetic defects, may harm an unborn child and may damage fertility.

Environmental Information Long-term toxicity to fish is expected to be minimal. It is also not expected to be toxic at the limit of water solubility. Coal tar pitch is immobile and does not appreciably leach to groundwater. It is also very poorly soluble in water. Coal tar pitch that is released or disposed in the environment is likely to remain unchanged for many years. When coal tar pitch is seen in soil, it is usually present as distinct pieces or chunks of black, hard material, which is not likely to be contacted in the same way as is soil. Exposure Coal tar pitch is an industrial product and is not sold directly to consumers or for direct consumer use.

Exposure to coal tar pitch is primarily limited to occupational settings, such as tar distillation, roofing and aluminum smelting. In these settings, occupational exposure to liquid, solid, heated or vaporous coal tar pitch is controlled by the use of enclosed processing systems, industrial hygiene controls and personal protective equipment. Each industrial facility should also have a thorough training program for employees and appropriate work processes, as well as safety equipment in place to limit exposure. Workers should follow the recommended safety measures in the relevant Safety Data Sheet (SDS). Information Sources Data is compiled from a variety of sources, including publicly available documents, internal data and other sources such as, but not limited to, Safety Data Sheets (SDS). For additional information regarding this product, including its physical and chemical properties, transport information and regulatory information, please refer to the applicable Safety Data Sheet (SDS).

2 Materials and methods

2.1 Materials

In the present work, was evaluated the influence of carbon swelling in obtaining coal binder. The main materials used as a feedstock during the process were:

- Samples of coal from Chadansky (Republic of Tuba), in figures 7 and 8 we are going to observe, with better quality, the coal samples that were used as raw material. Beside, in the table 4 and 5 we can see the approximate an ultimate characterization of the coal respectively.



Figure 7 – coal sample in solid state



Figure 8 - sample of powdered coal

Coal sample	Petrographic parameters, %					
Coal sample	Vt	Sv	Ι	$\sum OK$	R _{o,r}	σ_{R}
Average	85	3,07	10	13	-	-

Table 4 - Petrographic analysis of coal

Table 5 - Elemental composition of coal sample

	Proximate, %			Ultimate, % in <i>daf</i>			Atomic relation		
Sample	Wa	A ^d Ash content	V ^{daf}	$S_t^{\ d}$	С	Н	N	0	H/C
Coal	0,6	3,07	38,2	0,25	88,50	6,16	0,97	4,12	0,84

In the follow table 6, we can see the primary properties of the bituminous coal certified by the laboratory of the Siberian Federal University (Appendix 1).

Table 6 - Coal tar report

Type of sample	Name of analysis	Unit of measurement	Normative	Result of analysis
	Density at 20 °C	Kg/m3	GOST P 57037	1185.84
	Mass fraction of water	%	GOST 2477	1.7
Coal tar	Mass fraction of salt	%	GOST 1038	0.11
	Mass fraction insoluble in toluene	%	GOST 28357	7.1
	Mass fraction insoluble in quinoline	%	GOST 10200	3.9

- Final solution of petroleum products (Heavy Gas Oil (HGO) taken from the Fluid Catalytic Cracking (FCC) unit of the Omsk's refinery, itself, it is a mixture between pure HGO and decant oil), in the figure 9, we can see the sample which was used during the whole process and in the table 7, we can observe the main properties test of the HGO compared with the normative result:

 Table 7 - Laboratory Test Data for Heavy Gas Oil from FCC

Luboratory Test Data for Heavy			
Test	Normative	Result by normative	Result obtained
Density at 15 ° C, kg / m3, not less	ГОСТ Р 51069	1013	1042.01
Density at 20 ° C, kg / m3	ГОСТ 3900	-	1038.32
Carbon residue (micromethod), wt%, no more	ASTM D 4530	9	4.92
Kinematic viscosity at 50 ° C, mm2 / s, no more	ГОСТ 33	50	52.50
Correlation index, not less	ТУ 38.301-19-87-97 п 5.2	102	104.3
Mass fraction of water,%, no more	ГОСТ 2477	0.2	Traces
Mass fraction of mechanical impurities,%, no more	ГОСТ 6370	Not standardized result required	0.028



Figure 9 - Sample of HGO

In addition to the analysis of properties of HGO, an infrared spectrometry analysis was performed, as we can see in the following table 8 and figure 10:

Compounds	Content,%	Sum of aromatic components,%
Aliphatic hydrocarbons	75,5	
Diaromatic hydrocarbons	8,6	22.4
Diaromatic hydrocarbons	13,8	,
Asphaltenes	2,1	

Table 8 - Data of HGO infrared spectrometry

This information from infrared spectrometry allows us to identify the high percentage of aliphatic compounds that it presents in HGO with almost 76%, and a total of aromatic compounds of 22.3% which will serve as a point of comparison when analyzing the infrared results. spectrometry of the pitches obtained.

Finally, for the whole raw material, the table 9 show us the characterization of them.

Table 9 - Elemental composition of samples and solvents

Sample	C%	H%	N%	S%	O%	Ash,%
Heavy gas oil (HGO)	90,94	8,65	<0,3	<0,5	0,64	0
Coal tar	91,80	5,16	1,22	<0,5	1,42	0,1

2.2 Methods used

2.2.1 Determination of Ash content

Therefore, the preparation of the samples was carried out according to GOST 10742 and GOST 23083. To determinate the ash content of coal (3.07), an analytical sample was used, crushed to a particle size passing through sieve with a mesh size of 200 microns (0.2 mm). If is necessary, bring the sample to an air-dry state by spreading it in a thin layer for the minimum time necessary to achieve an approximate equilibrium of the mass fraction of the ventilation hood with the laboratory atmosphere. Before the starting the determination, the analytical sample is thoroughly mixed for minutes, preferably mechanically.

The procedure was started, putting the samples in the crucibles, making the measurements, and then the crucibles with coal were placed in the muffle furnace. At room temperature (22 °C), raised the furnace temperature to 500 °C within 60 minutes and maintained this temperature for 60 minutes. Continued heating to (815±10) °C in the same oven and kept at that temperature not less than 60 min. The figure 11 show us the moment of the drying of the samples.



Figure 11 - Drying of samples

Coal swelling is a phenomenon associated with physical and morphological changes that occur when coal is steeped in a particular solvent. Coal may be considered as a cross-linked polymeric macromolecule that may allow particular solvent molecules to penetrate the flexible framework. Analysis of the changes to the coal and solvent during swelling can provide valuable structural information on the coal, and facilitate more efficient use of this coal. Firstly, we crushed our coal to a particle size passing through sieve with a mesh size of 125 microns (0.125 mm).

2.2.2 Ultrasonic cavitation

This apparatus was carried out after our initial sample of coal tar, was put in contact with its respective solvent, in order to facilitate the swelling of the coal and improve its action, the sample was heated to a temperature of 60 C by means of a bath of water, and immediately cavitation was used for 30 minutes as the figure 12 show us.



Figure 12 - Cavitation of the sample

It is important to prioritize the mixing of the sample once the cavitation is finished, preferably manual.

2.2.3 Pyrolysis

Pyrolysis is most commonly used in the treatment of organic materials. It is one of the processes involved in charring wood. [28] In general, pyrolysis of organic substances produces volatile products and leaves a solid residue enriched in carbon, char. Extreme pyrolysis, which leaves mostly carbon as the residue, is called carbonization. Pyrolysis is considered as the first step in the processes of gasification or combustion.

Pyrolysis is one of various types of chemical degradation processes that occur at higher temperatures (above the boiling point of water or other solvents). It differs from other processes like combustion and hydrolysis in that it usually does not involve the addition of other reagents such as oxygen (O2, in combustion) or water (in hydrolysis). [29] Pyrolysis produces solids (char), condensable liquids (tar), and uncondensing/permanent gasses.

Thus, after the selection of the solvents, the obtaining process will be carried out through the pyrolysis; which will represent the 15% in the final solution before pyrolysis after his swelling. this process was carried out through the furnace as shown in figures 13 and 14.



Figure 13 - Final assembly in the laboratory



Figure 14 - Furnace assembly diagram

Where:

- 1. Furnace
- 2. Reactor
- 3. Refractory screen
- 4. Removal of gaseous and liquid coking products
- 5. Alonge
- 6. Three-neck round bottom flask
- 7. Reflux condenser

In this part, modifications will be made to change the temperature and residence time parameters, which allows us to obtain better information about the behavior of carbon at that temperature:

- raise the temperature to 320 ° C in 50 min
- keep the temperature of 320 ° C for 1 hour
- raise the temperature to 400 $^{\circ}$ C as soon as possible
- keep the temperature of 400 $^\circ$ C for 3 hour

When the pyrolysis step is finished, must be extract the product obtained from the container that is inside the vessel, thus, taking into account that the pitch obtained is in the solid state, the sample was heated to a temperature between 200 ° C - 250 °, with this temperature it is ensured that the structural composition of the bonds in the final pitch will not be modified, just simply decrease in viscosity will be obtained which will allow us an easy extraction of the pitch without damage or alterations to it.

2.2.4 Softening point

Softening point, is the temperature at which a material softens beyond some arbitrary softness. It can be determined, for example, by the Vicat method (ASTM-D1525 or ISO 306), Heat Deflection Test (ASTM-D648) or a ring and ball method as we can see in the following figure 25 and the one which was used (ISO 4625 or ASTM

E28-67/E28-99 or ASTM D36 or ASTM D6493 - 11). The follow figure 15, show us the apparatous used durint the determination of softening point.



Figure 15 - Softening point apparatus

The resins are noncrystalline amorphous materials that soften gradually over a range of temperatures. Therefore, the softening point is controlled by the average molecular weight of the resin. The softening point is also related to the intrinsic viscosity, hardness, and brittleness of resins.

ASTM D 3461-76, DIN ISO 4625. This method is the most frequently used to determine the softening point of resins and was used in this work. Show above figure 16 illustrates the experimental device used to determine the Ring and Ball Method R&B softening point.



Figure16 - Ring and Ball Method R&B

The resin is melted into a metal ring and left to cool. The ring is placed in a special metallic device, which is placed into a water or glycerol bath. A steel ball of given diameter and mass is placed on the ring and the bath is heated at a given rate. The temperature at which the ball forces the softening resin downward is noted as the softening point.

2.2.5 Determination of coke residue

Carbonaceous materials for the production of aluminum - Pitch for electrodes - Determination of coking value ISO 6998, was used in this work. This is an International Standard specifies a method for determination of the coking value of pitches used for the production of aluminum. Heating of a test portion under defined conditions at 550 f 10 $^{\circ}$ C and weighing the coke residue.

If the sample is sufficiently hard, crush with a small jaw crusher and grind it in a mortar to pass at least a 300 pm mesh sieve and, if possible, a 212 pm mesh sieve. If the ambient temperature is high, the operation will be facilitated by chilling the sample beforehand. In the figure 17, we can see the furnace which was used for the coke residue determination.



Figure 17 - Coke residue determination

If the pitch is too soft to crush, melt the sample and take sufficient of the molten mass for the test. The melting temperature shall not exceed 150 $^{\rm O}$ C and the melting period shall not exceed 10 min. It is also possible to transfer the required portion of a soft pitch directly to the porcelain crucible, without preliminary treatment.

2.2.6 Toluene insoluble determination (TI)

Standard Test Method for Toluene-Insoluble (TI) Content of Tar and Pitch (Short Method) ASTM D4312 - 20. This test method covers the determination of toluene insoluble matter (TI) in tar and pitch. Since this test method is empirical, strict adherence to all details of the procedure is necessary.

Therefore, the sample is digested, then extracted with hot toluene in an alundum thimble. The insoluble matter is dried and weighed.

2.2.6.1 Apparatus

- Extraction Apparatus—Flask with metal cap condenser as shown in figure 18.



Figure 18 - Extraction Apparatus

- Extraction Thimble, Alundum AN 485 coarse (formerly RA 98), 30 mm in diameter by 80 mm in height with flat bottom.

- Thimble Cover—Paper cone, made by wetting with water a 70-mm filter paper normally folded in a small glass funnel, and drying the funnel in an oven with the paper cone in place.

- Sieves, U.S. Standard 600-µm (No. 30) and 250-µm (No. 60).

- Heater, having a minimum capacity of 300 W per unit.

2.2.6.2 Dehydration of Sample

Hard Pitch—If the solid bulk sample contains free water, air-dry a representative portion in a forced draft oven at 50°C. Soft Pitch—If the presence of water is indicated by surface foam on heating, maintain a representative portion of the bulk sample of a temperature between 125 and 150°C in an open container until the surface is free of foam. Take care not to overheat, and remove heat source immediately when foam subsides. Tar—Dehydrate a representative portion of the bulk sample at atmospheric pressure using a simple side-arm distillation apparatus similar to the one in Test Method D 850 and stop the distillation when the temperature reaches 170°C. Separate any oil from the water that has distilled over (if crystals are present, warm sufficiently to ensure their solution) and thoroughly mix the oil with the residual tar in the still after the latter has cooled to a moderate temperature.

As an alternative to dehydration, the water content of the tar is determined by Test Method D 95 and, if the water content is less than 10 mass percent, the TI content is corrected to a dry-tar basis. This alternative method applies only to stable emulsions of water in tar, that is, no water separates when the tar sample is left undisturbed for 24 h at room temperature.

2.2.6.3 Apparatus used

In the figure 19, que can observe the apparatus which was used during the extraction step during this work.



Figure 19 - Extraction column

2.2.7 Quinoline insoluble

Standard Test Method for Determination of Quinoline Insolubles (QI) in Tar and Pitch by Pressure Filtration. This standard is issued under the fixed designation D 4746.

This test method covers the determination of the quinoline-insoluble matter (QI) in tar and pitch by pressure filtration and gives results comparable to those obtained by Test Method D 2318 or GOST 10200 83. Centrifugation method, for this method was used the centrifuge showed in the figure 19 and 20.



Figure 19 - Centrifuge SETA



Figure 20 - Inside the centrifuge

2.2.8 Infrared (IR) Spectroscopy

Infrared spectroscopy, due to the ideal range of wavelengths, is one of the most versatile methods for studying the structure of chemical compounds. Infrared radiation with a frequency of less than 100 cm⁻¹ is absorbed by an organic molecule and is converted into the energy of its rotation, and radiation in the range of about 10,000 - 100 cm⁻¹ is converted into the energy of vibrational motions of atoms in the molecule.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher energy near-IR, approximately 14000-4000 cm⁻¹ (0.8-2.5 μ m

wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately 4000-400 cm⁻¹ (2.5-25 μ m) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400-10 cm⁻¹ (25-1000 μ m), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these sub regions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

2.2.8.1 Spectroscopic Techniques

The infrared and near infrared analysis were performed on the original commercial feedstock samples at 25 °C. A Nicolet 380 FT-IR spectrometer from liquid phase (thin film) was used for the IR analysis. Wavenumbers from 4000 to 400 cm-1 were scanned. The samples were placed in an ATR-cell (Attenuated Total Reflectance) with a KBr crystal. The spectrometer was equipped with a fiber optic sampling probe for transflectance measurements. The wavelength region was set to 1100-2200 nm, and the total number of scans per spectra set to 64. Total path length was 2 mm. The spectroscopic data were then analyzed later using Unscrambler 7.6.

2.2.8.2 Theory of IR

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling.

In particular, in the Born-Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are determined by the normal modes corresponding to the molecular electronic ground state potential energy surface. Nevertheless, the resonant frequencies can be in a first approach related to the strength of the bond, and the mass of the atoms at either end of it. Thus, the frequency of the vibrations can be associated with a particular bond type.

In order for a vibrational mode in a molecule to be "IR active," it must be associated with changes in the permanent dipole.

A molecule can vibrate in many ways, and each way is called a vibrational mode. Linear molecules have 3N - 5 degrees of vibrational modes whereas nonlinear molecules have 3N - 6 degrees of vibrational modes (also called vibrational degrees of freedom). As an example H₂O, a non-linear molecule, will have $3 \times 3 - 6 = 3$ degrees of vibrational freedom, or modes. The following figure 21, we can observe a typical graph of a typical IR.



Figure 21 – example of isoprene (2-Methyl-1,3-butadiene) IR

Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g. N_2 , the band is not observed in the IR spectrum, but only in the Raman spectrum. Unsymmetrical diatomic molecules, e.g. CO, absorb in the IR spectrum. More complex molecules have many bonds, and their vibrational spectra are correspondingly more complex, i.e. big molecules have many peaks in their IR spectra.

3 Results and discussion

3.1 Determination of ash content

Firstly, we considered samples of coal from: Chadansky (Republic of Tuba) in order to determinate ash content (inert material) which should be less than 0.400 %.

Following the procedure, three samples were prepared, were put into crucible, and their respective mass was measured before they entered the oven, and after the heating process had finished, as shown in the table 10.

Sample	Mass Crucible, gr	Mass Crucible with Coal, gr	Mass Crucible with ash after heating, gr
1	19.4798	20.9852	19.5258
2	20.1026	21.609	20.1493
3	20.1627	21.6534	20.2085

Table 10 - Measurements	of	sampl	les
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According to the information obtained from table 6, the ash content was calculated through the following equation:

% Ash content =
$$\frac{W_3 - W_1}{W_2 - W_1} \times 100$$
 (1)

Where,

 W_1 = Mass Crucible

 W_2 = Mass Crucible with Coal

 $W_3 =$ Mass Crucible with ash after heating

The table 11, shows us the content of inert material of our coal, the homogeneity of the sample is observed by having a weighted average of 3.073% of ash content.

Table 11 - C	alculation of	ash content
--------------	---------------	-------------

Sample	Ash Content %
1	3.05
2	3.1
3	3.07
Average	3.073

In order to prepare our samples, were divided into seven test tubes with a ratio of 1: 3 (1 ml of coal per 3 ml of solvent) and for each tube, a different solvent was used as the following table 12 shows:

 Table 12 - Weight of coal samples and solvent samples

	-		
Sample Coal weight, gr (in 1 ml)		Solvent	
1	0.5280	1-Methyl-2-pyrrolidone (C ₅ H ₉ NO)	
2	0.5088	Diethylene glycol (C ₄ H ₁₀ O ₃)	
3	0.5278	Toluene (C7H8)	

Sample	Coal weight, gr (in 1 ml)	Solvent	
4	0.5009	Tetrahydrofuran(C ₄ H ₈ O)	
5	0.5004	Quinoline (C ₉ H ₇ N)	
6	0.5027	Methanol (CH ₃ OH)	
7	0.5023	Butanol (C ₄ H ₉ OH)	

The volumes of each test tube were measured each week, as shown in table 13, to determine the percentage increase in coal during swelling with the specific solvent.

Solvent	First week (ml)	Second week (ml)	Increase, %	Decrease, %
1-Methyl-2-pyrrolidone (C ₅ H ₉ NO)	1.35	1.4	40	-
Diethylene glycol (C ₄ H ₁₀ O ₃)	0.95	0.9	-	10
Benzol (C ₆ H ₆)	1	1.05	5	-
Tetrahydrofuran(C ₄ H ₈ O)	1	1.05	5	-
Quinoline (C ₉ H ₇ N)	1.1	1.2	20	-
Methanol (CH ₃ OH)	0.8	0.8	-	20
Butanol (C ₄ H ₉ OH)	0.8	0.8	-	20

Table 13 - Coal increase and decrease

Thus, with the results shown in the table 4, it is observed that the solvents that generated some positive change in the carbon swelling were: (40%) 1-Methyl-2-pyrrolidone (C_5H_9NO), (20%) Quinoline (C_9H_7N), (5%) Benzol (C6H6), Tetrahydrofuran(C4H8O); which will be used during the obtaining of carbon binder.

3.2 Pyrolysis

3.2.1 Sample preparation

Three processes were carried out, in which the first sample prepared was 100% (40 grams) of crushed carbon (without solvent); the second sample prepared was 50% (20 grams) of crushed carbon and 50% (20 grams) of 1-Methyl-2-pyrrolidone (first solvent) and the last sample prepared was 50% (20 grams) of crushed carbon and 50% (20 grams) of crush

Samples	Solvent	Coal weight measured	Solvent weight measured
1	Without	20 gr	-
2	1-Methyl-2-pyrrolidone	20 gr	20.19 gr
3	Quinoline	25 gr	28 gr

Table 14 - swelling of samples

In samples two and three, the carbon and the solvent were put for three days in a closed vessel, to promote swelling. In addition, the sample one was directly used in the next step because no solvent for swelling was used. For each sample, in order to promote the pyrolysis, was used ultrasonic cavitation machine. the sample is heated to a temperature of 60 $^{\circ}$ C for 30 min, once the heating is finished, the cavitation process is started for 40 min, thereby ensuring the thermal dissolution of some long chains within the carbon structure, and favors the action of the solvent on swelling.

3.2.2 Adding the solution

To finalize the sample preparation, the 100% final solution was a mixture predetermined between the solution of our swollen carbon (15%), and a final solvent (85%), which is composed of:

- The first 50% is Heavy Gas Oil (HGO) taken from the Fluid Catalytic Cracking (FCC) unit of the Omsk's refinery, itself, it is a mixture between pure HGO and decant oil.

- The second 50% is Coal tar from Altaykocs.

Therefore, to continue action of the pyrolysis and the action of the solvent, 15% of swollen carbon after cavitation and 85% of the final solvent (HGO + CT) are mixed with the help of a mixer and a heater at an average temperature of 60 ° C, for approximately 20 minutes. In the following table 15, you can see the measurements of the solvent and the carbon solution before entering the process of obtaining our final pitch.

Sample	Swollen Carbon, gr	Final Solvent (HGO+CT), gr	Vessel, gr	Vessel Solvent + Coal
1	20	127,5	108,75	256,45
2	15.06	85,05	99,50	199,17
3	15,23	85,5	99,48	200,21

Table 15 - Weights before thermal process

It is important to clarify that sample one aims to receive a total product of 150 grams, on the contrary, samples one and two had 100 grams as objective.

3.2.3 Final assembly

An attempt was made to simulate the conditions of the industry in the laboratory, for this, as we can see in the figure 23 a closed steel container (reactor) with a single gas outlet was used, in order to collect the condensates. The closed steel container was put into a furnace, then, subjected to the following heating parameters:

- raise the temperature to 320 $^{\circ}$ C in 50 min

- keep the temperature of 320 ° C for 1 hour

- raise the temperature to 400 $^{\circ}$ C as soon as possible

- keep the temperature of 400 $^\circ$ C for 3 hour

The final assembly can be observed in the figure 24, in which the gas outlet is connected with a round bottom flask with two necks, connected to a condenser, the bottom flask is submerged in a bowl of water in order to help the condensation of distillate coming from our vessel. To verify the quality and usefulness of the products obtained, for main tests were carried out after the thermal cocking:

3.3 Softening point determination and coke residue determination

Softening point determination was carried out, extracting the carbon binder obtained from the production vessel, a process in which it is necessary to heat the pitch to an average temperature of 200 $^{\circ}$ C in order to obtain a liquid state from it.

Cocking residue, this test was carried out, messuring one (1) grams per two samples of pitch in a crucible previously dried and putting samples of our product into a furnace for 2 hour and half at 550°. The following table 16, allows us to observe the data obtained in the different samples, and to compare the different products obtained. Therefore, the percentage of efficiency in each process can be observed:

Experiment number:	Solvent for swelling	Final solution* (gr)	Pitch obtained (gr)	Condensate obtained (gr)	Softening point T°	Coke residue %
1		147.72	53.22	19.55	55.75	56
2	1-Methyl-2- pyrrolidone	99.67	55.19	18.72	45.85	43
3	Quinoline	100.73	48.37	43.87	60.2	51

Table 16 - Products obtained

* final solution, 15% of swollen carbon after cavitation and 85% of the final solvent (HGO + CT)

From the table 16, Among the three products obtained, the one with the closest properties to the pitches used today is the one obtained with the quinoline solvent, which has a softening temperature close to 60 degrees centigrade and a coke residue of 51. These data They confirm that the swelling of the carbon through the use of solvents can modify the properties and quality of the same during the production of the pitches. Nevertheless, the product obtained with the solvent 1-Methyl-2-pyrrolidone got the lowest result of softening point and coke residue, which indicate not good quality if we would like to use it in industry process. The pitch obtained by using Quinoline, present the closest properties compared with some type of pitch used in the industry like Type A.

3.4 Mass balance of the first production pack

It is important to observe the mass percentage between the product received and the distillate obtained during the pyrolysis process and the losses, as we can see in table 17.

Experiment Number	Pitch, % wt	Distillate, % wt	Gas + Losses, % wt
1	36.02	13.23	50.75
2	55.37	18.78	25.85
3	48.01	43.55	8.44

 Table 17 - Mass percent including solvent influence

In addition, it is important to keep in mind that in the mass flow, it is not important for our study to take into account the contribution of the solvent used in the swelling of the carbon. Therefore, as shown in table 18, the mass flow without including the contribution of the solvent used during the swelling of the carbon allow us to identify how much percentage we had of losses.

<u></u>			
Experiment Number	Pitch, % wt	Distillate, % wt	Gas + Losses, % wt
1	38.95	14,31	46.74
2	59.86	20.31	19.83
3	51.92	47.08	1

Table 18 - Mass percent not including solvent influence

From the table 18, we can analyze that the yield of pitch is higher through using 1-Methyl-2-pyrrolidone even though this product has the worst quality results in softening and coke residue. It clear that, the lowest yield of pitch was without using of any solvent and present the biggest losses compared with the other pitch produced.

Due to the fact that the pitches so far show a physical appearance very similar to the pitch used in the industry, but the results of softening point and coking residue were not the desired ones; It was decided to modify the methodology at the time of preparing the sample. It was decided that before performing the cavitation process, a mechanical mixing of the solution had to be carried out for 30 minutes, then the cavitation equipment had to be set at a temperature of 50 °C.

3.5 Production of the second pitches pack

A mechanical mixing of the solution had to be carried out for 30 minutes, then the cavitation equipment had to be set at a temperature of 50 ° C, after 30 min of cavitation, the mixture was carried out with the final solvent, but in this case a mixer was used and no heating was carried out ° C The following table 19 shows the results products of three in which they were used as solvent: new (1)Tetrahydrofuran(C_4H_8O). (2) Benzol (C_6H_6), (3) 1-Methyl-2-pyrrolidone (C_5H_9NO) and (4) without solvent.

Experiment number	Solvent for swelling	Coal,- 15%, gr	Solution (Coal tar + HGO), 85% , gr	Solution before pyrolysis, gr	Pitch obtained, gr	Distillate obtained, gr
1	Without	19.27	109.19	130.42	70.22	58.04

Table 19 - Second pack of pitch obtained after methodology corrections

Experiment number	Solvent for swelling	Coal,- 15%, gr	Solution (Coal tar + HGO), 85% , gr	Solution before pyrolysis, gr	Pitch obtained, gr	Distillate obtained, gr
2	Tetrahydrofuran (C ₄ H ₈ O)	19.93	112.93	132.86	60.89	62.19
3	Benzol (C ₆ H ₆)	19.56	110.84	130.4	59.38	53.37
4	1-Methyl-2- pyrrolidone (C ₅ H ₉ NO)	19.99	113.63	156.22	84.69	57.06

According to the information shown in the table 19, for the production of the second package of pitches (the four previously named solvents), an average of coal swelled feed was approximate 20 grams used, which represent the 15% of the final solution before to start the thermal process. Moreover, an average of solution (Coal tar + HGO) 135 grams, which represent the 85% of the final solution before to start the thermal process in each pack.

It is important to clarify that a pitch was made without using any solvent in the carbon swelling phase, to be able to compare how each solvent affects the properties of the final product or pitch.

3.6 Mass balance of the second production pack

In addition, it is important to keep in mind that in the mass flow, it is not important for our study to take into account the contribution of the solvent used in the swelling of the carbon. Therefore, as shown in table 20, the mass flow without including the contribution of the solvent used during the swelling of the carbon allow us to identify how much percentage we had of losses.

Experiment Number	Pitch, % wt	Distillate, % wt	Gas + Losses, % wt
1	51.8	42.5	5.7
2	43.8	44.8	11.4
3	45.5	40.9	13.6
4	54.2	36.5	9.3

Table 20 - Mass balance of the second pitches pack not including solvent influence

According with the information from the table 20, the highest pitch's yield was obtained by using 1-Methyl-2-pyrrolidone (C_5H_9NO) during the swelling step with 54.2 %, which close to the pitch's yield obtained without the using of any solvent and the lowest pitchs yield was obtained by using Tetrahydrofuran (C_4H_8O). The lowest losses and gas yield were obtained for the pitch without using any solvent (5.7%), followed by the (9.3) obtained with 1-Methyl-2-pyrrolidone (C_5H_9NO), then the (11.4) with Tetrahydrofuran (C_4H_8O) and the last, and biggest losses by (13.6) with Benzol (C_6H_6). Moreover, the process using Tetrahydrofuran (C_4H_8O) and Benzol (C_6H_6) presented a close yield of pitch with 45% approximate, distillate with 43%.

With these pitches, the analyzes of: coke residue, softening point, insoluble toluene and insoluble quinoline were carried out, the data can be observed in the following table 21.

Solvent	Softening point °C	Coke residue %	Toluene insoluble, % wt	Quinoline insoluble, % wt
Without	96.2	46.8	32.3	3.38
Tetrahydrofuran (C ₄ H ₈ O)	105.1	51.9	37.7	3.1
Benzol (C ₆ H ₆)	94.9	47.7	29.7	2.8
1-Methyl-2- pyrrolidone (C ₅ H ₉ NO)	54.1	36.5	36.1	1.87
Coal tar pitch (Industrial)	109.4	57.8	27.5	13.1

Table 21- Pitches analysis results

According with the information from the table 21, the pitch obtained by using Tetrahydrofuran (C₄H₈O) got the highest softening point with 105.1 °C, the highest result in toluene insoluble with 37.7 %, the highest coke residue with 51.9 % and Quinoline insoluble with 3.1%, all these properties comparing only the pitches obtained by the using of some solvent.

3.7 FT-IR test results

In an organic molecule, an atom constituting a chemical bond or a functional group is in a state of constant vibration, and its vibration frequency is equivalent to the vibration frequency of infrared light [28,29]. Therefore, when the organic molecules are irradiated with infrared light, the chemical bonds or functional groups in molecules could be absorbed by vibration. Different chemical bonds or functional groups absorb different frequencies, and will be in different positions of infrared spectrum.

3.7.1 FT-IR for Pitches

Therefore, the chemical bonds or functional groups information is contained in molecules could be obtained. The infrared spectrum curves of four pitch samples are shown in Fig. 22-25.

Since those four pitch coal are obtained from same methodology, and the use of the same raw materials, the metamorphism degree and coal structure types between them are similar.





In the analysis of microstructure, the infrared spectrum curve is generally divided into four parts for peak fitting analysis. The functional groups and bonding types in the 3000–3600 cm–1 band are mainly hydroxyl and hydrogen bonds. However, the hydrogen bond has little reference value to the coal microstructure for this experiment, so it is ignored in subsequent experiments. [29,35]



Figure 23 – FT IR of pitch-like product with Tetrahydrofuran



Figure 25 – FT IR of Pitch-like product with 1-Methyl, 2- pyrrolidone

2500

3000

54.17745

1000

wave number, cm⁻¹

500

540.74074

1500

2000

0,2

0,1

0,0

4000

534,53919 3416,3652

3500

The wave number ranges from 2700 cm-1 to 3000 cm-1, which are mainly the characteristic peaks of methyl and methylene vibration. The stretching vibration and

antisymmetric stretching vibration of methyl group mainly appear near 2851 cm-1 and 2946 cm-1. The stretching vibration of the methylene group mainly appear near 2909 cm-1. The content of aliphatic hydrocarbons in coal structure could be preliminarily determined by calculating the peak area value in this region. Wavelengths between 1000 cm-1 and 1800 cm-1 are the vibrational wave bands of most main oxygen-containing functional groups in coal structure, including carboxyl, ruthenium, methoxy and ether groups. [33]

Therefore, it is important to analyze the infrared spectrum curves of this section to understand the oxygen-containing functional groups in coal. The aromatic skeleton vibration (-C=C-) appearing near 1600 cm-1 basically reflects the total aromatic content in coal, which is the main data for studying the degree of aromatization in coal structure and aliphatic-aromatic ratio. The wave number in the range of 700–900 cm-1 are the concentrated position of aromatic ring absorption peaks, which reflects the aromatic hydrogen content in coal. Meanwhile, the ratio of aromatic hydrogen to total hydrogen atoms is a significant parameter for the basic coal structure.

In infrared absorption spectroscopy, the light directed onto the sample covers a range of frequencies in the infrared region of the electromagnetic spectrum. This type of absorption spectroscopy is most useful for the identification and analysis of organic compounds. We have classified based on the peak wave number in the table 22.

Wave range (cm ⁻¹)	Wave num. (cm ⁻¹)	Meaning of the absorption peak		
	3535	Free hydroxyl		
2000-2600	3529	Hydrogen bond		
5000-5000	3415	Phenolic hydroxyl		
	3040 - 3050	C-H aromatic bonds		
2920		Methyl symmetric stretching vibration		
2700-3000	2850	Methylene symmetric stretching vibration		
	1600	C=C skeleton vibration of aromatic		
1000-1800	1436	asymmetrical deformation vibration of CH ₂		
	1370	symmetrical deformation vibration of CH ₂		
	1250	C-O on the phenyl ether		
	836	Aromatics with 1 substitutions		
700-900	806	Aromatics with 4 substitutions		
	742	Aromatics with 3 substitutions		

Table 22 - Main infrared peak wave number and its representative meaning

In general, aromaticity was defined as the proportion of hydrogen or carbon atoms existing in a coal as part of an aromatic ring structure. The aromaticity index by hydrogen (H_{ar}) was calculated based on intensities of bands correspond to aliphatic and aromatic structures. It took into account that the ratio of the extinction coefficient of stretching vibrations of C-H aromatic bonds to the extinction coefficient of aliphatic C-H bonds was 0.20, while the ratio of the extinction coefficient of stretching vibrations of $-CH_2$ - groups and $-CH_3$ groups was 0.5 [31,32]. H_{ar} indexes were estimated by formula:

$$H_{ar} = \frac{A^{3050}/_{0.2 \times A^{2920}}}{1 + (A^{3050}/_{0.2 \times A^{2920}})} , \qquad (2)$$

Where A^x is the absorption of an appropriate band which correspond to aromatic or aliphatic C–H bonds. Therefore, for each pitch the calculation of Har index was:

$$H_{ar}(Without solvent) = \frac{\frac{0.07608}{0.2 \times 0.11148}}{1 + (\frac{0.07608}{0.2 \times 0.11148})} = 0.77$$

$$H_{ar}(Tetrahydrofuran) = \frac{\frac{0.0882}{0.2 \times 0.12439}}{1 + (\frac{0.0882}{0.2 \times 0.12439})} = 0.78$$

$$H_{ar}(Benzol) = \frac{\frac{0.08225}{0.2 \times 0.13829}}{1 + (\frac{0.08225}{0.2 \times 0.13829})} = 0.75$$

$$H_{ar}(1, Methyl, 2, pyrrolidone) = \frac{\frac{0.08191}{0.2 \times 0.13561}}{1 + (\frac{0.08191}{0.2 \times 0.13561})} = 0.75$$

The ratio of A^{2950} to A^{2920} , which can characterize the average length of aliphatic substituents in COM [16]. The Tetrahydrofuran present the higher aromaticity index by hydrogen (H_{ar}) with 0.78 compared to pitch results without solvent. The aromaticity index between benzol and tetrahydrofuran is the same with 0.75, but compared to the pitch without solvent they are 0.02, which means that it is not a significant difference. Nevertheless, it is clear that all of the pitches present a close value of H_{ar} but the utilization of tetrahydrofuran as the solvent for swelling make it possible to obtain the pitch-like product which characterized by maximum level of aromaticity. The difference is not significant but such pith-like product showed the maximum level of coke residue.

It can be seen from the spectra that N-Methyl-2-Pyrrolidone can react with compounds from reacting mixture because FTIR spectra of appropriate pitch like product contains pick at ≈ 1500 cm⁻¹ which indicate presence of heterocyclic pyrrole-

like compounds. This is most likely that N-Methyl-2-Pyrrolidone interact with coal organic matter during swelling step because it was reported about possibility of such interaction.

Other bands correspond to N-contained structures are the similar or very close to those for O-contained structures, which are present in coal organic matter and solvents too. It is not possible to use them for analysis. Table 23 and 24 shows the results of FT-IR data processing.

Course la				Wave N	lumber			
Sample	742	810	839	1032	1238	1260	1374	1437
Without solvent	0.661	0.330	0.215	0.084	0.057	0.034	0.092	0.208
Tetrahydrofuran	0.710	0.355	0.240	0.086	0.056	0.032	0.099	0.229
Benzol	0.726	0.374	0.240	0.097	0.065	0.041	0.101	0.240
1-Methyl-2- pyrrolidone	0.726	0.374	0.240	0.097	0.066	0.041	0.101	0.240

Table 23 - FT-IR data processing of pitches (724 – 1437)

				Wave	Number			
Sample	1600	1645	2854	2918	2951	3042	3411	3535
Without solvent	0.191	0.040	0.145	0.190	0.111	0.076	0.016	0.005
Tetrahydrofuran	0.210	0.034	0.155	0.199	0.124	0.088	0.025	0.005
Benzol	0.215	0.047	0.180	0.230	0.138	0.082	0.019	0.010
1-Methyl-2- pyrrolidone	0.215	0.047	0.180	0.230	0.136	0.082	0.018	0.010

These data represent the absorption peaks of an appropriate band during the infrared spectrometry test, observing that Benzol and 1-Methyl-2-pyrrolidone present a similar composition in their content of aromatic with 1/3/4 substitution, asymmetrical and symmetrical deformation vibration of CH₂ and C-H aromatic bonds. As we previously determined with the aromaticity index, however, these two pitches show a lower content of C-H aromatic bonds, CH₂ and C=C than the pitch obtained

without the presence of any solvent. The relative absorption was estimated and is showed in the table 25 and table 26:

Comple		Wave Number										
Sample	742	810	839	1032	1238	1260	1374	1437				
Without solvent	3.453	1.722	1.122	0.437	0.298	0.180	0.483	1.085				
Tetrahydrofuran	3.374	1.685	1.139	0.408	0.268	0.153	0.469	1.088				
Benzol	3.381	1.740	1.120	0.454	0.302	0.190	0.470	1.116				
1-Methyl-2- pyrrolidone	3.381	1.740	1.120	0.454	0.307	0.190	0.470	1.116				

Table 25 - Relative absorption (724 – 1437)

Table 26 - Relative absorption (1600 - 3535)

Community.		Wave Number									
Sample	1600	1645	2854	2918	2951	3042	3415	3535			
Without solvent	1	0.207	0.758	0.992	0.583	0.398	0.082	0.008			
Tetrahydrofuran	1	0.164	0.735	0.947	0.591	0.419	0.119	0.020			
Benzol	1	0.219	0.840	1.070	0.644	0.383	0.087	0.045			
1-Methyl-2- pyrrolidone	1	0.218	0.839	1.065	0.632	0.382	0.084	0.046			

From the table 25 and 26, it is clear that was used the A^{1600} to determinate the relative absorption because of the standard and the main compounds are aromatics compounds which are in this range of absorption. It can be seen from the tables that pitch-like products with tetrahydrofuran has the maximum amount of phenolic hydroxyl (\approx 3400). May be it is due to thermal transformation of tetrahydrofuran or chemical reactions between TGF and another constituents of reaction mixture. High concentration of hydroxyl as well as high aromaticity can increase amount of coking residue. Influence of O-contained compounds presents consists in softening point of binder material increasing. However, it was reported that oxygen in carbon binder can increase viscosity significantly that is not good for technological using.

In addition, it can be confirmed by the information in these tables, the structural similarity during the absorption range (742-1600) between the pitches obtained with benzol and 1-Methyl-2-pyrrolidone, excluding groups C-O on the phenyl ether (1238)

in which 1-Methyl-2-pyrrolidone presented higher absorption, however, they present differences between the groups of Hydrogen bond (3535), Phenolic hydroxyl (3415), and Methyl (2950) or Methylene (2840). It is important to confirm that the presence of solvents obviously structurally modifies the composition of the pitch, and directly affects its properties. Taking account all the above, one of the reasons of the low softening point of the 1-Methyl-2-pyrrolidone, could be the presence of N-contained groups.

3.7.2 FT-IR of pitches after toluene insoluble TI

It is important to clarify that the following results are of pitches after an insoluble toluene test. Therefore, it is important to compare and analyze how this process affects the final composition of the product. The infrared spectrum curves of four pitch samples are shown in Fig. 26-29:



Figure 26 – FT IR of Pitch-like product with without solvent (IT)







Figure 28 – FT IR of Pitch-like product with Benzol (IT)



Figure 29 – FT IR of Pitch-like product with 1- Methyl, 2- pyrrolidone (IT)

From the figure 28, the aliphatic functional group (2700–3000 cm⁻¹), presented a higher value of vibration, which mean that could be a problem with the sample like contamination. However, from the without solvent, it's clear that Tetrahydrofuran (IT) and 1-Methyl-2-pyrrolidone (IT) present a higher absorption in the range of C-H aromatic bonds, which is going to be reflexed in the index of aromaticity, the relationship between these aliphatic group is typical and present normal values of vibration. Table 27 and 28 shows the results of FT-IR data processing pitches after toluene insoluble TI.

		Wave Number							
Sample	748	810	839	1035	1170	1260	1376	1439	
Without solvent	0.551	0.394	0.327	0.209	0.209	0.111	0.188	0.428	
Tetrahydrofuran	0.747	0.504	0.432	0.132	0.209	0.122	0.165	0.453	
Benzol	0.070	0.086	0.047	0.051	0.022	0.056	0.113	0.254	

Table 27 - FT-IR data processing of pitches after toluene insoluble TI (724 – 1439)

				Wave I	Number			
Sample	748	810	839	1035	1170	1260	1376	1439
1-Methyl-2- pyrrolidone	0.781	0.491	0.384	0.161	0.218	0.116	0.194	0.486

Table 28 - FT-IR data processing of pitches after toluene insoluble TI (1600 - 3425)

C 1.		Wave Number						
Sample	1600	1650	1735	2855	2918	2951	3040	3425
Without solvent	0.603	0.140	0.025	0.443	0.680	0.394	0.192	0.248
Tetrahydrofuran	0.670	0.126	0.029	0.292	0.460	0.303	0.245	0.162
Benzol	0.125	0.076	0.019	0.627	1.213	0.720	0.047	0.124
1-Methyl-2- pyrrolidone	0.601	0.173	0.030	0.430	0.622	0.360	0.220	0.227

From the table 27 and 28, the Tetrahydrofuran pitch had presented the highest value of absorption in the aromatic groups, C-O on the phenyl ether and asymmetrical deformation vibration of CH_2 . Thus confirmed, its high aromaticity index due to the fact that after testing insoluble toluene, its composition is richer in aromatic compounds than the other pitches. It took into account that the ratio of the extinction coefficient of stretching vibrations of C-H aromatic bonds to the extinction coefficient of aliphatic C-H bonds was 0.20. H_{ar} indexes were estimated by formula (2):

$$H_{ar}(Without solvent) = \frac{\frac{0.1916}{0.2 \times 0.3943}}{1 + (\frac{0.1916}{0.2 \times 0.3943})} = 0.71$$

$$H_{ar}(Tetrahydrofuran) = \frac{0.2447/_{0.2} \times 0.3026}{1 + (0.2447/_{0.2} \times 0.3026)} = 0.80$$

$$H_{ar}(Benzol) = \frac{0.0468/_{0.2 \times 0.7198}}{1 + (0.0468/_{0.2 \times 0.7198})} = 0.25$$

$$H_{ar}(1, Methyl, 2, pyrrolidone) = \frac{\frac{0.2202}{0.2 \times 0.3599}}{1 + (\frac{0.2202}{0.2 \times 0.3599})} = 0.75$$

The Tetrahydrofuran present the higher aromaticity index by hydrogen (H_{ar}) again with 0.80 presenting a high increase with 0.1 more than the results obtained by the pitch without solvent. Even the 1-Methyl-2-pyrrolidone presented value higher than without solvent by 0.04 with 0.75. Nevertheless, it is clear that Benzol present a poor value of H_{ar} with 0.20, meaning that could be a problem with the sample during the test or maybe the solid sable was not enough. The relative absorption was estimated and is showed in the table 29 and 30:

C a marcha		Wave Number						
Sample	748	810	839	1035	1170	1260	1376	1439
Without solvent	0.915	0.653	0.543	0.347	0.347	0.184	0.311	0.709
Tetrahydrofuran	1.115	0.752	0.645	0.197	0.313	0.182	0.247	0.676
Benzol	0.560	0.688	0.373	0.407	0.174	0.445	0.903	2.041
1-Methyl-2- pyrrolidone	1.300	0.818	0.639	0.267	0.363	0.193	0.323	0.810

Table 29 – Relative absorption of IT pitches (724 – 1439)

Table 3	30 - 100	Relative	absor	ntion	ofIT	nitches ((1600 -	3425)
radic .	50 -	Relative	ausor	puon	0111	phenes	(1000 -	54257

Course la	Wave Number							
Sample	1600	1650	1735	2855	2918	2951	3040	3425
Without solvent	1	0.233	0.042	0.735	1.129	0.654	0.318	0.412
Tetrahydrofuran	1	0.188	0.043	0.436	0.687	0.452	0.365	0.242
Benzol	1	0.612	0.149	5.030	9.732	5.774	0.375	0.994
1-Methyl-2- pyrrolidone	1	0.289	0.044	0.716	1.036	0.599	0.366	0.378

From the table 26, it is clear that was used like in the table 24, the same value of absorption A^{1600} to determinate the relative absorption because of the standard and the main compounds are aromatics compounds which are in this range of absorption. It is also clear to observe that in this case, could be easily observed that the results obtained with tetrahydrofuran present more controlled values between the range of the

peaks in the section between (1450- 2950), which indicates which indicates the high presence of groups such as:

- Methylene symmetric;
- C=C skeleton of aromatic;
- asymmetrical deformation of CH₂;
- symmetrical deformation of CH₂;

It was impossible to determinate the bond between the absorption and extraction, because we have not enough information about the coefficient of extinction. The characteristic absorption peak data could be characterized by the following formula:

$$I_1 = \frac{A_{V(CH_2)} + A_{V(CH_3)}}{A_{V(C=C)}}$$
(3)

$$I_2 = \frac{A_{V(CH_2 + CH_3)}}{A_{V(C=C)}}$$
(4)

$$I_{3} = \frac{A_{V(-OH)} + A_{V(C-O)}}{A_{V(C=C)}}$$
(5)

$$I_4 = \frac{A_{V(CH_2)}}{A_{V(CH_3)}}$$
(6)

Where, I_1 represents the hydrogen richness and hydrocarbon generation potential in pitch structure, I_2 denotes the aliphatic to aromatic ratio in pitch molecule, while I_3 indicates the oxygen enrichment degree of the functional group, I_4 reflects the alkane side chain length to some extent.

The infrared spectrum peak data of four pitches samples are calculated and arranged. Results are shown in Table 31 and 32:

Sample	I1	12	13	I4
Without solvent	1.569	0.784	0.241	0.445
Tetrahydrofuran	1.558	0.779	0.189	0.431
Benzol	1.587	0.794	0.237	0.422
1-Methyl-2- pyrrolidone	1.587	0.794	0.237	0.422

Table 31 - Calculation results of infrared spectral parameters for pitches

Sample	I1	I2	13	I4
Without solvent	1.021	0.510	2.236	0.439
Tetrahydrofuran	0.923	0.461	1.328	0.366
Benzol	2.944	1.472	2.232	0.443
1-Methyl-2-pyrrolidone	1.132	0.566	1.961	0.399

Table 32 - Calculation results of infrared spectral parameters for pitches after IT

From the table 31, on the hydrogen-rich degree parameter I_1 , the trend of Benzol and 1-Methyl-2-pyrrolidone > Without solvent > Tetrahydrofuran is presented. The I1 values of Benzol and 1-Methyl-2-pyrrolidone are 1.16% higher than those of Without solvent, respectively. It indicates that the hydrogen richness of Benzol and 1-Methyl-2-pyrrolidone is larger than that of Without solvent and Tetrahydrofuran. The hydrocarbon generation potential indicates incompleteness of thermal transformation. It means that pitch-like product with 1-Methyl-2-pyrrolidone has the high amount of aliphatic chains. Such feature can decrease softening point along with other reasons explained previously.

For the calculation results of aliphatic-aromatic ratio I_2 , it shows that Tetrahydrofuran < Without solvent < Benzol and 1-Methyl-2-pyrrolidone. The Tetrahydrofuran pitch, after the partial aliphatic structure in the pitch is detached from gaseous alkane, the proportion of aliphatic in pitch structure decreases, resulting in a lower aliphatic-aromatic ratio than the pitch without solvent. It could be seen from the calculation results of I_1 and I_2 that, the Tetrahydrofuran pitch has the characteristics of small hydrocarbon generation potential, high ablation of small molecules (e.g. alkanes) and relatively small waxes.

From the table 32, the index I_3 reflects the oxygen enrichment of pitch. According to the results of elemental analysis, it can be seen that the oxygen element content of the benzol pitch sample is higher than the pitch without solvent. Nevertheless, the 1-Methyl-2-pyrrolidone pitch and Tetrahydrofuran pitch are lower than the pitch without solvent with 12 % and 40% less respectively.

The $-CH_2$ - is commonly found in the pitch structure of alkane side chain, alicyclic and aromatic ring bridges. And $-CH_3$ as a terminal group, mainly occurs at the end of the alkane side chain. Therefore, the calculation results of infrared spectrum I₄ value of the pitch could to some extent reflect the length of aliphatic hydrocarbons side chain in the pitch structure. Calculation results of I₄ present the order of Benzol > Without solvent >1-Methyl-2-pyrrolidone > Tetrahydrofuran, from which, it was observed that the proportion of $-CH_2$ - in Tetrahydrofuran pitch is shorter than $-CH_3$, indicating that the aliphatic alkanes have not longer side chains in the pitch like a

product with Tetrahydrofuran. It can indicate that tetrahydrofuran addition help to crack aliphatic chains during pyrolysis which results in high cocking residue and high softening point.

CONCLUSION

It has been shown that the use of coal tar and petroleum products as raw material allowed us to receive binder coal with properties which are very close to the materials currently used in the industry. For this purpose, it can be carried out through pyrolysis of the following components (85% of Coal tar and Heavy gas oil, 15% swollen coal) at the temperature of 400 °C, that simulate the real conditions.

Through the data received, it is reflected that it is possible to control the properties and compositional structure of the pitch like a product while the initial coal is swollen with the appropriate solvent.

The pitch-like a product obtained with tetrahydrofuran, presented a softening temperature 105.1°C, which indicates a 9% of increase than the pitch like a product obtained without the use of solvents. Moreover, obtaining a higher value of the aromaticity index by hydrogen (Har) with 80% and characterized by the increase of the coke residue with respect to the pitch like a product without solvent.

Comparing the pitch like a product received without solvent and the pitch like a product recived with solvent have shown that the pyrolysis of the swollen coal leads to interaction between the use of solvent and the reaction mixture (Coal, Coal Tar, Heavy Gas Oil), that interaction may be the reason for the differences between the molecular composition of the non-swollen coal and the swollen carbon.

It could be seen that the proportion of -CH2- in the pitch like a product with Tetrahydrofuran is shorter than -CH3, indicating that the aliphatic alkanes have not longer side chains in the Tetrahydrofuran pitch. It can indicate that tetrahydrofuran addition help to crack aliphatic chains during pyrolysis which results in high cocking residue and high softening point.

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APPENDIX 1



Федеральное государственное автономное образовательное учреждение высшего образования «Сибирский федеральный университет»

Институт нефти и газа

Лаборатория нефти и нефтепродуктов

Юридический адрес: 660041, г. Красноярск, пр. Свободный, д.79

№ 32/18

Протокол

результатов испытаний

«12» апреля 2018 г.

1.

Наименование заказчика: ООО «РУСАЛ ИТЦ»

2. Юридический адрес заказчика: 660111, Российская Федерация, г. Красноярск,

улица Пограничников, дом 37 строение 1

- 3. Наименование образца: Смола каменноугольная для переработки А сорт 2
- 4. Дата поступления пробы: 15.02.2018 г.
- 5. Место отбора пробы: ООО «МеталлПромСервис»
- Количество отобранных образцов: <u>1,0 дм³</u> из них для испытаний <u>1,0 дм³</u> из них для контрольных образцов – нет
- 7. Методы консервации нет
- 8. Особые условия отбора нет
- 9. Регистрационный номер пробы: 5206
- 10. Дата проведения испытаний: 09.04.18-12.04.18 г.
- 11. Результаты испытаний

Номер пробы	Наименование Работ	Ед. изм.	НД на метод испытания	Результаты испытаний образца (пробы)
Смола	Плотность при 20 °С	кг/м ³	ГОСТ Р 57037	1185,84
каменноуголь	Массовая доля воды	%	ГОСТ 2477	1,7
ная для	Массовая доля золы	%	ГОСТ 1038	0,11
переработки А сорт 2	Массовая доля нерастворимых в толуоле	%	ГОСТ 28357	7,1
	Массовая доля нерастворимых в хинолине	%	ГОСТ 10200	3,9

Исполнитель: Заведующий лабораторией:

/ <u>А. А. Чумаков/</u> / <u>Д. В. Агровиченко/</u> / <u>И. В. Савич/</u> Federal State Autonomous Educational institution Higher education "SIBERIAN FEDERAL UNIVERSITY" INSTITUTE OF OIL AND GAS Chemical technology of natural energy carriers and hydrocarbon materials

APPROVED Head of the Department F.A. Buriukin » Oh 2021.

MASTER'S THESIS

Alternative carbon binders on the basis of petrochemical and coal feedstock 04.04.01 Chemistry 04.04.01.10 Petroleum chemistry and refining

data

signature, data

Ph.D., Associate Professor

S.A. Vladimir

C.M. Brian

Research supervisor

Graduate

Krasnoyarsk 2021

Federal State Autonomous Educational institution Higher education "SIBERIAN FEDERAL UNIVERSITY" INSTITUTE OF OIL AND GAS Chemical technology of natural energy carriers and hydrocarbon materials

APPROVED Head of the Department ____F.A. Buriukin » Ch 2021. ds

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Ph.D., Associate Professor S.A. Vladimir

C.M. Brian

Krasnoyarsk 2021