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MASTER´S THESIS

Modelling of Carbon Binder Obtaining in Flow Reactor

04.04.01 Chemistry
04.04.01.05 Petroleum Chemistry and Refining

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ABSTRACT

Throughout the years, the industrial production of aluminum has not stopped growing due to the high increase in demand that adds even more uses than it originally already enjoyed. The sources from which it is extracted from nature seem inexhaustible, due to this, the numerous investigations that have been done in this field, rather than increasing its production, are focused on carrying it out in a cleaner, more efficient and sustainable way since it causes high contamination in its manufacturing process, especially by substances that are highly dangerous such as benzo[a]pyrene that is generated from the use of carbon anodes and more specifically in the binders used to manufacture these anodes.

Among the proposals to minimize the emission of pollutants is to search for new materials that replace the polluting raw materials, being made from recycled materials, biomaterials or heavy oil fractions. These types of materials have lately been studied in various research centers, however in most of the works these are carried out by means of an experimental laboratory methodology without the use of technology or a computerized system that allows variations to be obtained to obtain more results. fast and with a high proximity value.

Technological advance in computers together with the development of programs, and current computer science together with fundamental mathematics and its applications, are very intense fields but with great importance. The different math programs that interact with the computer in its different applications are very broad, especially for solving very complicated numerical problems whose manual algebraic resolution would have been practically impossible to do a few years ago. This is why this work will be focused on obtaining a simulation of the most representative properties of the synthesis process, with the aim of contributing to the growth of this emerging field with a view to a larger scale of production of binders that serve for the production of carbon anodes in the aluminum manufacturing process.

Keywords: CARBON BINDERS, COAL TAR, COKING COAL, ANODES, SOFTENING TEMPERATURE.

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INTRODUCTION

In the future the industry may be determined by low capital and operating cost processes. The reliability and low price of mineral coal are the factors for its use in industrial processes, it has been used in many and diverse activities. The relentless pressure on operating, production and investment costs is forcing the various industries that use coal to accelerate technological development and consider new technologies and improvements, with a view to better qualities, better performance, less capital intensity and better environmental impact.

Although innumerable efforts have been made to reduce dependence on coal worldwide, this is one of the main products in energy production, metallurgical industry, ceramic industry, etc., achieving, contrary to what was expected, an increase of 1.5% in its production since 2014 according to the International Energy Agency (AEI) with a production very close to 8 billion tons in 2019.

Worldwide, new reserves have been discovered, mainly in the large producing countries, measured at more than one billion tons. One of these large producers is Russia, which is in 6th place on a list led by China, producing around 430 tons in 2019. Russia is home to the second largest coal reserves in the world, after the United States, with an estimated 162,000 million tons located mainly in the Siberian basins [1].

One of these uses that can be given to these carbonaceous materials and their by-products is the production of binders, the most widely used is coal tar, which is obtained as a by-product of the coking process. This process also generates a large amount of by-products and secondary chemicals, such as methane and other hydrocarbons, transforming the coke into "water gas". When heating the coal the yield in solid products (coke), liquids (tar) and gases, varies with the temperature. From 1,000 °C the coke is graphite [2].

However, in recent years studies are being carried out to dispense with this binder, since coal tar is a by-product of coal coking, which is a highly expensive process. Coke is used as a reducing agent in the production of steel, a process that takes place in iron smelting furnaces, where the carbon from the coke combines with the oxygen from the iron ore to convert or "reduce" the iron oxide. to pure iron, casting that is carried out in the blast furnace [3].

Currently, 73% of the world's steel comes from the Blast Furnace route; However, this percentage has been decreasing in recent years due to the development of other much less expensive technologies that reduce or eliminate the need to use coke, such as the production of steel by direct reduction with hydrogen and natural gas or the use of electric arc furnace (EAF) that are fed mainly on scrap steel. A great example of this imminent change is represented by the US, which produced 67% of its total steel production in 2017 through the EAF process. As a result of the above, the United States accounted for only 1.6 % of world demand for metallurgical coal during the same period, as this was not very relevant in its steel production process [4].

As the demand for coke decreases, the demand for coal tar will in turn increase, so it will become scarcer, in turn increasing its price, since, contrary to coke, coal tar is a product that is growing in demand [5], demanding increasingly higher quality standards due to its implementation in the development of new technologies for carbon materials or aluminum production processes (Hall-Heroult process) [6].

Aluminum is obtained from alumina by means of an electrolytic process in which the anodes are made up of a charred mixture of petroleum coke (filler) and pitch (binder), generally coal tar. The nature of these anodes, and, more specifically, the composition of the constituent pitches, is related to one of the main problems of this method of aluminum production: the emission of polycyclic aromatic hydrocarbons (PAH), many of which are carcinogenic [7].

The preparation of such carbon anodes begins with the mixture (called paste) of the filler coke and the binder pitch that is carried out at a temperature above the softening point of the pitch (which is usually of the order of 90-100 °C), and this operation constitutes the first point of PAH emission into the atmosphere. The second point is constituted by the electrolytic process itself, in which temperatures of the order of 950 °C are reached, especially in the so-called Söderberg technology, in which the carbonization of the paste formed by coke and pitch takes place in situ, in the electrolytic cells. During this carbonization, significant PAH emissions can also occur.

Faced with this problem, the need to develop new processes that allow obtaining a high-quality binder product such as coal tar without going through the costly coking process is almost mandatory, in addition to avoiding or reducing the problems that this process generates of impact environmental [8].

Russia also has large oil fields whose by-products can easily compete with traditional coal, producing a type of coal with greater reactivity in thermochemical processes, being also less polluting to the environment, reducing carcinogenicity. However, this type of petroleum-derived products, such as pitch, has several disadvantages that are associated with a high content of volatile substances, low coking capacity or low content of substances insoluble in toluene that are responsible for the binding properties carbon [9]. The use of petroleum pitch in pitch and coke compositions gives them less plasticity and also increases their viscosity, which is why their use for the production of anodes and electrodes widely used in the metallurgical industry is not convenient.

The solution to this problem is to use a mixture of these two substances, both coal tar and petroleum products (pitch), in order to obtain a binder material that meets the demanding quality criteria.

This type of solution has already started with various research works, one of them that of Safin et al., which is the basis of this work, obtained a material that meets quality criteria. These results were achieved starting from three raw materials in equal quantities such as petroleum-derived (commercially available product from Omsk refinery), coal tar (CT) from Altai-Koks plant and a 1GZh medium-range coking coal with high volatility, under defined pressure and temperature conditions in an oxygen-free atmosphere [10].

The implementation of a computerized system of this process in a continuous flow reactor will allow greater control of the variables involved as well as being able to predict the changes that could eventually occur in the start-up of the process (on pilot scale), reducing the greatest number of setbacks, allowing to gain experience quickly with a reduced cost and without jeopardizing the productivity of the system. Few are the innovative companies in this sector of the production of high-quality coal raw materials, one of them is Yancoal from Australia which has a pilot scale production of 350 kg/h equivalent to a quantity in the range of 1-2 kt / year, so it would be a great opportunity to be one of the pioneers in the production of this type of raw material at the country level [11].

1.1 Background study

Various authors and research groups have dedicated their efforts to improve the production of carbon binders for various industries mainly producing anodes, cathodes and graphite electrodes. Most of the bibliography at present focuses on studying the properties of coal tar as the only binder that can be commercialized on a large scale, there is a shortage of studies focused on new materials that can replace its high consumption or at least reduce it. This is due to the fact that the production of coal tar depends on industrial processes that have been replaced over the years with the application of new technologies, in addition, this binder has a relatively high amount of harmful compounds that can seriously affect living organisms with which may have contact. For this reason, works whose purpose is to synthesize or adapt new materials that can serve as raw material in the production of binders are shown below.

1.1.1 Laval University - Canada

Hussein, et al., try to synthesize a binder called bio-pitch that is mainly used for use in the aluminum industry and whose main characteristic is that it does not use non-renewable raw materials such as coal tar in order to reduce the ecological footprint that these types of industries that produce this material leave behind. They produce binders from the pyrolysis of biomass, obtaining a biological oil which, when heat treated, achieves a product with characteristics similar to coal tar, with similar viscosity and softening point values.

This material meets the quality characteristics expected of a traditional carbon binder, possessing high wettability as well as complying with a standard behavior against thermal processes with a very good result capable of competing directly with commercial coal tar. Another reason why this binding material would be more beneficial is because it has a much lower value of sulfur, which reduces the contamination of this element into the environment due to its impact on global warming due to the effect greenhouse that produces. Additionally, reduced values of heavy metals such as vanadium and nickel.

The process in which it is obtained is based on the evaporation at atmospheric pressure of the volatile components of low molecular weight present in the biomass and on the polymerization of its higher molecular weight compounds, however the treatment of this material was carried out under a controlled heat treatment reaching a maximum temperature of 200 °C due to its high amount of oxygen to avoid possible unwanted sources of combustion that may affect the characteristics of the final product [12].

Although bio-oil, the base product in the production of bio-pitch, is an organic material, it comes from the pyrolysis of softwood, so it would still continue to be harmful to the environment and also a material with limited access when it is made with the waste of this wood, since it depends on other manufacturing processes for its production. For this reason, although it is a fairly reasonable and adequate alternative to current times, it would not meet the necessary demand required by the carbon binders consumer industry, which requires new methods or raw materials that may be applicable in production processes. current.

One of these substitutes or rather complements of coal tar that may be applicable today are the compounds derived from oil, more specifically heavy oil or heavy fractions that are obtained after obtaining the lighter fractions of crude oil such as gasoline, diesel, lubricating oils, etc. As in the work below carried out in the city of Krasnoyarsk and presented at a conference by Marakushina, et al.

1.1.2 International Conference “Aluminum of Siberia”

The primary objective of his research is to reduce the harmful effects it has on the environment when using coal tar for the production of anodes due to the release of benzo[a]pyrene gas into the environment when they are consumed during the production of metallic aluminum. In addition to reducing the content of benzo[a]pyrene, which is the most toxic compound, a material with a low content of sulfur and ash is obtained as it does not have high amounts of heavy metals. To achieve this, they propose the substitution of a fraction of coal tar for a fraction of petroleum derivatives as a complement in obtaining this binder.

During the experimentation, two different types of petroleum-derived compounds are tested, such as heavy gas oil from the catalytic cracking unit and a heavy resin from pyrolysis. These two types of compounds were used due to their similarity in chemical composition and physical properties to coal tar.

With the use of this type of heavy petroleum compounds, a binder that is possible to be used in the production of anodes was predicted as results and also reduces the emissions of benzo[a]pyrene by 20 to 40%, however its properties characteristics are not the most adequate to be able to compete with the tar coal that has a superior quality according to the authors.

A more in-depth comparison of this type of materials is presented below where Korean researchers from Chungnam National University analyze the behavior of these raw materials in the production of thermal and electrical conductivity electrodes, which is another industrial use that can be given to this type of binders.

1.1.3 Chungnam National University

Jong, et al., focus their work on the comparison of a binder derived from petroleum with one of commercial characteristics based on coal. The experimentation consists of using these two substances as binders in the formation of electrodes in fixed molds, also using graphite and coke as raw materials, called fillers.

A suitable preparation of the particle size of the filler was taken into consideration in order to find a balance between its solidity and consumption of binder in the formation of electrodes. That is, by using a reduced particle size, its specific surface will be high and therefore it will require a greater amount of binder to cover this entire area. If the opposite happens and a larger particle size is used in the filler, the formation of the electrode will require less amount of binder, however, it will lose solidity [13].

Additional properties were found, which were already known, such as that when using the high softening point oil pitch, it will allow better filling of the empty spaces between the coke and therefore allow a greater thermal conductivity of the material, obtaining values of up to 102.8 W/mK compared to lower values when using the carbon base binder with a value of 99.5 W/mK. They also observed a direct relationship between the softening point and the thermal conductivity, obtaining higher values of this property the higher its softening point value, with values compared between 116 °C and 150 °C of the same oil binder.

The mass loss of the binders at the temperatures of the electrode formation process, around 900 °C, did not present representative values with losses of 2 to 3 % for the oil binder and losses of around 1 % for the binder. carbon-based. However, these results of mass loss are important when analyzing the durability of the electrodes since when using a binder with a greater amount of volatile fractions such as oil binder, they can affect the physical characteristics of the electrode as there is greater formation of intergranular spaces between the filler, not to mention that it will emanate a greater amount of gases that are harmful to the environment.

1.2 Objectives

1. Evaluate the synthesis of a new type of binder in a flow reactor in which raw materials such as coke, coal tar and a heavy oil fraction will be treated in order to analyze the optimal conditions for the process based on experimental results.
2. Determine the most important variables in binder production such as coke content, softening point, substances insoluble in toluene, pressure and viscosity as a

function of temperature using MATLAB R2019a as mathematical model processing software.

3. Reduce the degree of pollution to the environment that occurs due to the emanation of gases when the anodes are consumed that are produced when using only the coal tar as binder in its manufacture, because it has a considerable amount of benzo[a]pyrene.

4. Give added value to heavy oil fractions that can make possible large investments in the future in the binder's industry, anodes, due to the increasingly scarce production of coal tar.

5. Propose a design idea that allows it to be used for the production of this binder with greater flows of raw material on a pilot scale, which will be given by the realization of the PFD plan made with the AutoCAD Plant program in 2D and 3D.

1.3 Justification

The justification for this project is given by the fundamental objectives of this work, one of these is to reduce the environmental impact of producing materials that contain a high number of pollutants and, as previously explained, the use of materials such as coal tar causes subsequent contamination when used by industries that require it. Producing new types of materials and evaluating their sustainable production that allow the reduction of contaminants highly risky for life and the planet, will give the material a greater permanence in the industrial sector, which will allow it to be produced for a much longer period of time due to those new increasingly restrictive environmental laws are currently being enacted around the world.

Another reason is to take advantage of the great variety of natural resources that the Russian Federation possesses, especially in the region of Siberia where there is a large amount of production and reserves of coal and oil.

There is a great advantage in the new government plans to reactivate these industries to provide them with financing and technology with the aim that they can be the main producers of these resources but mainly of their derivatives since they give them an added value that will be more valuable for the world market. As an example, to mention one of these projects is the plan to reach the goal of 670 million tons per year of coal until the year 2035. In addition to belonging to one of the 8 countries with the largest oil reserves worldwide, it would start with a wide advantage by implementing factories that involve this type of studies for the creation of new materials and thus be able to achieve industrialization plans such as long-term goals.

2 Literature Review

In this section, the basic concepts that are involved in the development of the project will be treated, such as the review of the raw materials, their composition and their most representative characteristics, as well as the phenomena that intervene in this synthesis process together with the explanation of why that the different softwares with which it was worked have been chosen.

2.1 Coal Tar Pitch

Hydroformylation Coal tar is a by-product in the production of coke, it is a thermoplastic material obtained by carbonization of coal as a raw material at high temperatures, above 1000 degrees Celsius followed by a cooling of its volatile substances to a value lower than 400 °C [14]. Next, in Figure 1, shows the general molecular structure of this type of compound, while Figure 2, a diagram of the coal coking process is presented, in which the various by-products are found, of which the coal tar pitch stands out.

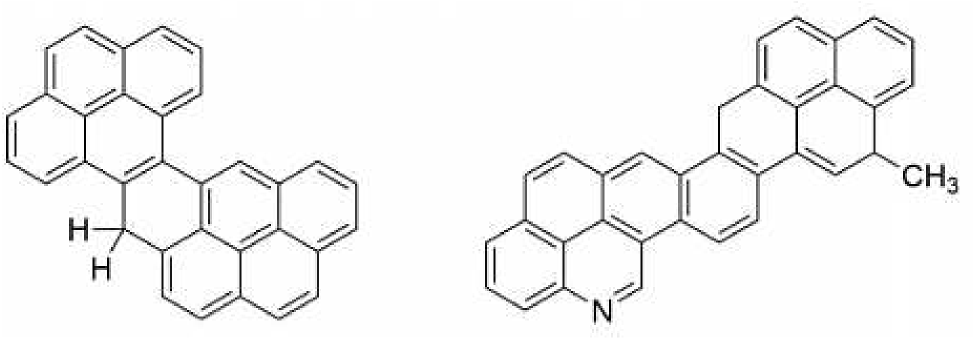


Figure 1 – Coal Tar, average molecular structure

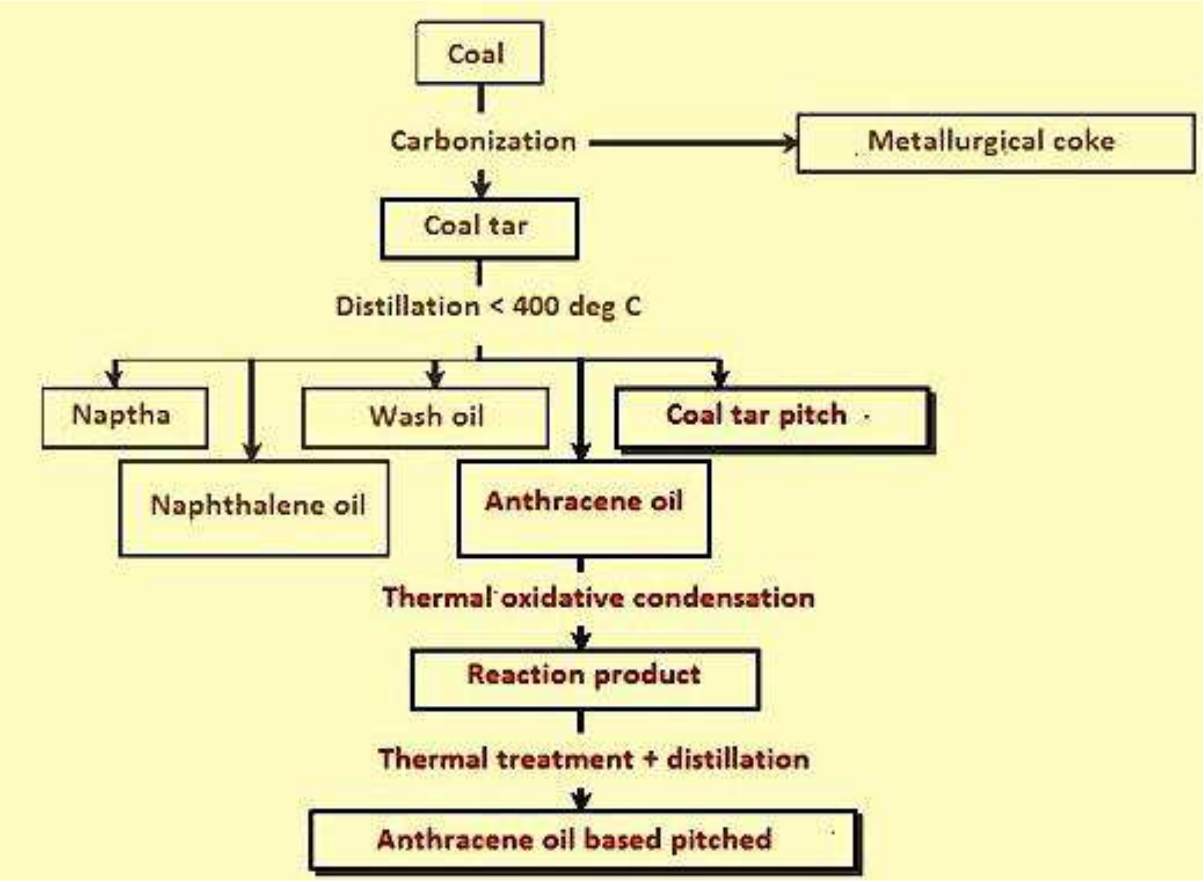


Figure 2 – Scheme for obtaining coal tar pitch in the coking process [15]

A thermoplastic material is one that is formed by polymers that are united by intermolecular forces or Van der Waals forces, forming linear or branched structures. For example, we can say that a thermoplastic material resembles a set of tangled ropes that we have on top of a table, the greater the degree of entanglement of the ropes, the greater the effort that we will have to make to separate the ropes from each other given to that the friction that occurs between each of the strings offers resistance to separate them, in this example the strings represent the polymers and the friction represents the intermolecular forces that hold them together [16].

Due to this property, this material is one of the most used and desired when requiring a binder for the production of anodes or cathodes in the metallurgical or energy industry in general, since the behavior of coal tar allows it to enter the pores. intergranular and form a paste with high stability that can withstand high process temperatures as well as the high pressures to which they are subsequently subjected in the formation of finished materials [17].

This property of forming paste with high stability is due to different properties that a binder of these characteristics must fulfill, these properties lie in the presence of molecular groups of oxygen and nitrogen, as well as in the values of surface tension and viscosity. Although both variables depend on the intermolecular forces of the substances, they are interdependent concepts [18].

There is a method with which the binding capacity of this pitch can be determined, called wettability, which is a very important interfacial characteristic in industries that deal with bituminous or petrochemical materials. This method consists of grinding the sample of the binder material that can be a coal tar to a mesh size of # 200 or its equivalent to 75 microns, then it is placed in an alumina crucible in which it is heated up to 178 °C. A Once it has been heated, the material is poured onto a surface where the material in which the binding characteristics will be evaluated is located. The measurement parameter consists of the assessment of the angle at which the binding material falls on the surface of the coke. Figure 3 shows the various measurements carried out during this analysis [19].

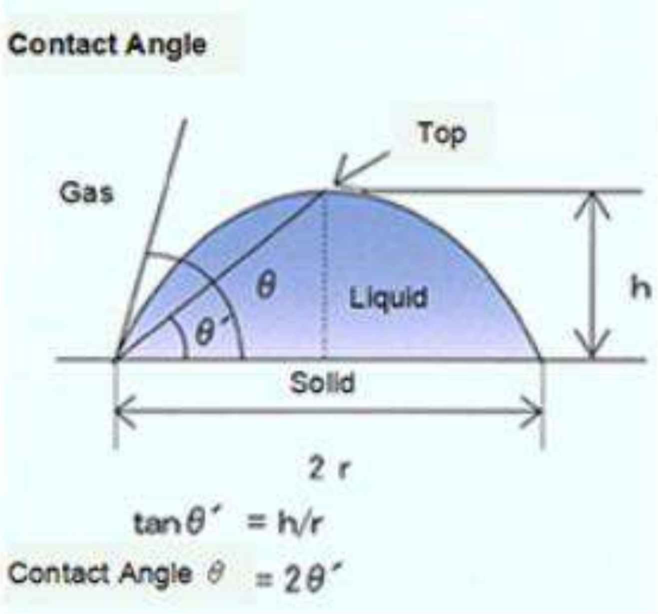


Figure 3 – Representation of the values for the calculation of wettability

There are several problems with the use of coal tar as a binder since it produces very dangerous substances for the human organism and for the environment in general, releasing compounds such as benzo[a]pyrene gas during the consumption of the anodes of which They are part of the process of obtaining metallic aluminum. This benzo[a]pyrene, which is shown in Figure 4, is a polycyclic aromatic hydrocarbon considered one of the most powerful carcinogens, gastrointestinal cancer, lung cancer and other types of cancer, as well as causing different conditions such as dermatitis, chest pain, low immunity and respiratory problems [20].

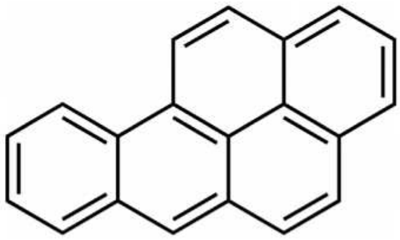


Figure 4 – General structure of Benzo[a]pyrene

2.2 Petroleum Derived Product

This work specifically deals with heavy oil derivatives, bituminous type because these types of substances are the ones that have a greater amount of compounds that can be converted to coke by means of thermal processes.

Most of the world's oil resources are viscous and heavy hydrocarbons, which are difficult and expensive to produce and refine. Generally, the heavier or denser crude oil, the lower its economic value. The lighter and less dense crude fractions, derived from the simple distillation process, are the most valuable. Heavy crude oils tend to have higher concentrations of metals and other elements, which requires more efforts and expenses for the extraction of usable products and the final disposal of waste [21].

However, with high demand and high oil prices, and with the production of most conventional oil fields in decline, the attention of the industry in many parts of the world is shifting towards the exploitation of heavy oil and the Instead of taking advantage of the heavy fractions that are obtained by refining light or medium crudes.

For example, in Figure 5, you can see the percentage of different types of oil in the total oil reserves worldwide, where heavy oil, extra heavy oil and bitumen make up approximately 70 % of the total oil resources in the world, equivalent to an estimated 9 to 13 trillion barrels [22].

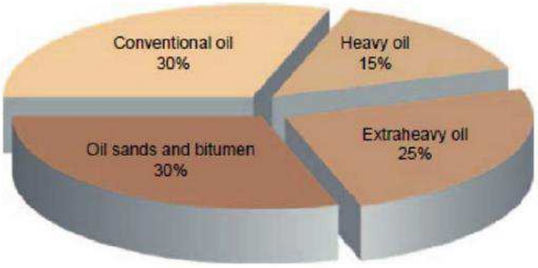


Figure 5 – Total oil reserves in the world

In oil refining processes, as in vacuum distillation or cracking process, a considerable amount of bitumen is obtained as a residue that will depend on the composition of the processed oil, this is considered one of the heaviest fractions that are produced during the conversion of crude to lighter products. Feedstocks used for the production of coke comprise:

- Petroleum Fluidized Catalytic Cracker Decant Oils (FCCDO):
- Petroleum Low-Sulphur Vacuum Residues (LSVR) or Vacuum Residues (VR).
- Coal-Tar Pitches (CTP).
- Ethylene Tar Pitches (ETP).
- Solvent Refined Coals (SRC).

FCCDO oil*:* is a heavy residue formed by catalytic cracking of VR, atmospheric residue, or a mixture of both. The main function of the catalytic cracking reaction is the production of naphtha: the greater the severity of the reaction, the more aromatic the FCCDO is. Less severe cracking conditions produce a greater abundance of long alkyl side chains attached to aromatic molecules, of which the vast majority of FCCDO is composed. The selection of the catalyst is highly influential on the subsequent quality of the coke formation, this is an aluminosilicate that will contribute to the ash content that the coke will contain. In its chemical composition, the FCCDO flow is characterized by high concentrations of polycyclic aromatic hydrocarbons (PAH) of> 70 %, with an insignificant concentration of reactive asphaltenes [23].

Vacuum Residue Petroleum (VR): is produced as the residual product of the vacuum distillation of atmospheric residues. Compared to other raw materials, they are generally composed of higher molecular weight compounds, also characterized by a high content of sulfur, asphaltenes and aliphatic molecules. This type of raw material produces coke of low quality but which is widely abundant in the market. LSVR can be used in a blend with a more aromatic settling oil to increase the quality of the one that will simultaneously produce a lower sulfur content coke. The ash content of LSVR or VR feedstocks is totally dependent on the mineral matter of the crude oil and the efficiency of upstream desalination [23].

Heavy oil compounds are very viscous material of black color that is practically a solid at temperatures below 40 °C soluble in carbon disulfide, has very little amount of volatile substances, waterproofing material and with a high composition of substances insoluble in toluene [24].

It is also called as a hydrocarbon material because it has a high carbon content in its chemical composition, equivalent to 87 % in addition to 11 % hydrogen and 2 % oxygen.

However, for the correct characterization of the properties of asphalt bitumens, an elemental chemical analysis is not enough, but a careful study of its physico-chemical properties is required, among these the viscosity, penetration test, thermal susceptibility, aging, penetration index, softening point. Each of these is explained below [25]:

Viscosity: It depends a lot on the temperature. At a lower temperature, bitumen has a high viscosity and acquires the properties of a solid body, while, with increasing temperature, the viscosity of the bitumen decreases and becomes a liquid state. There is no relationship with density although these properties are visually similar.

Penetration test: The degree of penetration is the unit of measurement of the consistency of the product. The consistency of a bitumen can vary depending on the environmental conditions, varying between liquid, semi-solid or solid. Consistency varies as the density of a bituminous product increases as the consistency decreases with increasing density.

Thermal Susceptibility: Although it is an originally solid product, it is in turn malleable. This is achieved through thermal variations. In this case, with the application of heat.

Aging: Bitumens are put into work in a liquid state. Then they harden and the viscosity grows. This phenomenon takes place until reaching a certain hardness. From there, the cohesion decreases and the product becomes brittle, very sensitive to abruptly applied stresses and rapid deformations.

Softening Point: As density increases, penetration decreases. This represents an increase in the softening point. A test for its measurement is the ring and ball test (A and B) which consists of increasing the temperature of the system composed of water or glycerin depending on the type of bituminous sample to be evaluated, the measurement consists of taking the temperature value at the point Exact when by the action of heating and by the weight of the ball on the sample it reaches the reference mark of the test, which is generally located at a distance of 25 mm. Figure 6 shows the experimental scheme used to determine the softening point [26].

Figure 6 – Softening point apparatus [27]

Figure 7, shows what the typical structure of a petroleum pitch is like, while Table 1, presents a summary of the properties and characteristics of a bituminous compound, and also a comparison with asphalt and tar [28].

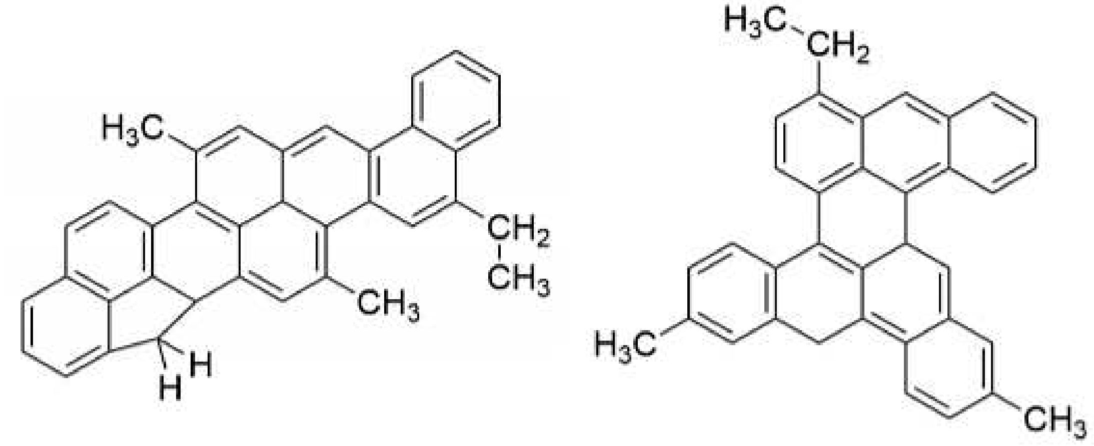


Figure 7 - Average structure of an oil pitch

Table 1 - Common physical-chemical characteristics of bituminous compounds

Density 20 °C (kg/m3)		1004,8
Coke capacity %		13,12
% V/V	Asphaltenes	3,5
	Resins	15,9
	Solid paraffins	1,7
	Paraffin-naphthenic hydrocarbons	24,6
	Aromatics	56
Vanadium		25,1
Nickel		34,9
Sulphur (% w/w)		1,35
Kinematic viscosity (cSt)		1038 (a 100 °C)
		337 (a 120 °C)

The main uses of commercially available bitumen are: Bitumen is used for making roofing and moisture-proof felts, for waterproof wrapping paper, asphalt for pipes, joint fillers, bituminous filler compounds for cable boxes, for sealing accumulators and batteries, dam protection felts and for thermal insulation materials for buildings, refrigeration equipment and cold storage [24].

Additionally, the use that will be given to these bituminous mixtures will be that of a binder for the production of aluminum anodes, for this the mixture of this compound will be made with the traditional coal tar, denominating petroleum coal tar. Petroleum coal tar.

2.3 Petroleum Coal Tar

Petroleum coal tar can contain a percentage of 15 % to 40 % by weight of the petroleum-derived product as a raw material in the production of the binder.

Currently, Russia does not produce this type of product due to various problems to eliminate in the properties of this material, such as presenting softening temperatures higher than those obtained with only the use of such coal, so it requires a greater energy consumption in subsequent use. In addition, these oil fractions have a lower amount of aromatic substances that are the precursors of the formation of coke in the binder, which is detrimental, not counting on the fact that as they are heavy fractions, it will contain a higher percentage of sulfur in its composition [29].

There are two methods for the production of this material, the first consists of the direct mixture of both components under mechanical agitation that produces a homogeneous mixture, while the second method consists of the joint distillation of the initial resins of petroleum and coal tar, thus reaching 50 % in the total mixture of these substances but with physical characteristics more similar to pure coal tar [30].

The binder to be obtained, in addition to obtaining these two components, which are the heavy oil fraction and coal tar, will also use coke to give it a higher percentage of this compound in the final product called pitch like product.

2.4 Coke

Coke is a low-impurity, high-carbon fuel, usually made from coal. It is the solid carbonaceous material derived from the destructive distillation of low-ash, low-sulfur bituminous coal.

Metallurgical coke is obtained by a process of coking, pyrolysis or destructive distillation (heating in the absence of air between 1000 and 1300 °C with a time of 15 to 30 hours, eliminating the volatile material) of bituminous mineral coals that have the capacity to transform into coke after going through a plastic phase. This process generally is carried out in chamber of 30 m^3 [31].

While coke can form naturally, the commonly used form is man-made. The form known as petroleum coke, is derived from petroleum refinery coke units or other cracking processes. Its main use is in smelting blast furnaces, where it must meet high hardness, good agglomeration and resistance to compression, in cast iron great mechanical resistance, great thermal performance, fluid and carburized cast iron, it is also used in masonry, factories. cement, lime and dolomite kilns, etc.

Among its uses are [32]:

- Coke is used in the preparation of producer gas which is a mixture of carbon monoxide (CO) and nitrogen (N2). Gas production occurs by passing air over hot coke. Coke is also used to make water gas.
- Coke is used as a fuel and as a reducing agent in the smelting of iron ore in a blast furnace. Carbon monoxide produced by its combustion reduces iron oxide (hematite) in the production of the iron product.
- Coke is commonly used as a fuel for blacksmithing.

Beehive ovens are used for its production, which help to guarantee the coking properties in the final product, metallurgical coke. Different transition stages of the coal are given until the coke is obtained as the desired final temperature for the process is reached, as explained below [33].

100 ºC – 200 ºC: Progressive elimination of humidity and release of gases.

350 ºC: Beginning of carbonaceous fusion.

425 ºC: End of melting and beginning of swelling.

450 ºC: Maximum swelling and maximum gas pressure.

600 ºC: Release of tar and gas formation.

625 ºC: Maximum evolution of ethane and initiation of small amounts of ethylene.

650 ºC: Greater weight loss.

700 ºC: Maximum evolution of hydrogen, carbon dioxide, ethylene and gases.

800 ºC: Rapid reduction of gases.

1100 º C: Gases evolved, carbon monoxide and hydrogen,

The chemical reaction that governs this process is:

$$\underset{\textbf{Coal}}{4(C_3H_4)_n} \rightarrow \underset{\textbf{Benzene}}{nC_6H_6} + \underset{\textbf{Coke}}{5nC} + 3nH_2 + \underset{\textbf{Lighter hydrocarbon}}{nCH_4}$$

A general diagram of the equipment used during this process is shown in Figure 8.

During this reaction, approximately 1400 lb of coke and 10 gallons of tar are produced for every ton of medium surface area coal [34].

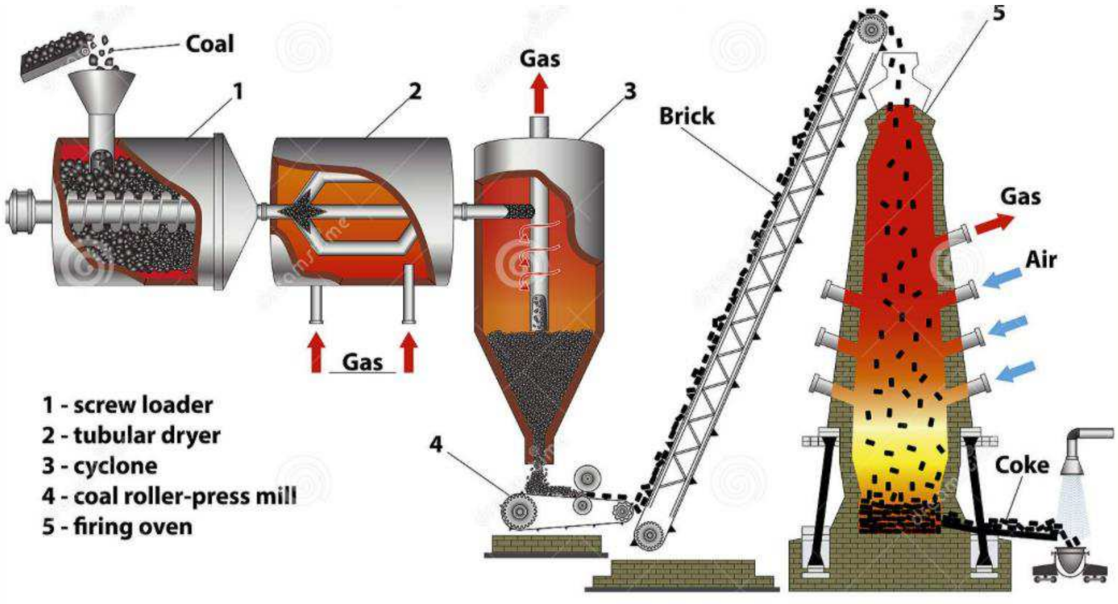


Figure 8 - General diagram of the process of converting coal to coke

The remaining factors to consider to obtain a high quality coke are; particle size, charge density, temperature, coking time, humidity and the aging of the coals during aging. Factors that will be detailed below:

Coals for the production of coke or coking coals granulometry: The finer the coke quality, for example in France 65-90 % < 2nm is used, in the United States between 70 % -80 % < 2nm is required. Generally, a particle size smaller than 3.15 nm gives better results by providing a better structure and hardness to the coke [35].

Charge density: It is the weight of the coal per cubic meter of retort, it influences the pressure on the walls of the retort; it is of order 0.8 ton/m3 at an industrial level; the higher the density, the production improves and there are larger sizes, the density is influenced by humidity and granulometry.

Coking process temperature: The coking temperature is an operational parameter, which drastically influences the quality of the coke obtained. That is, as the coking temperature increases, a better-quality coke will be obtained.

Coking time: As the coking speed decreases and the coking time increases, the mechanical resistance of the coke obtained improves (said time is a determining factor of the plant's capacity).

Humidity: The variation in the humidity of the coals leads to a variation in the charge density, and consequently the coke production yield. Due to the evaporation of the water the heating rate is reduced, increasing the coking time.

Aging of coals during storage: The storage of coals alters their coking properties by oxidation, presenting a higher incidence in coals with a high content of volatile matter. Within industrial limits, the impact on kiln productivity is very small.

In the process, several by-products are generated that are generally refined within the coke plant to basic chemicals such as elemental sulfur, ammonium sulfate, benzene, toluene, xylene and naphthalene [36].

Coke oven workers are exposed to polycyclic aromatic hydrocarbons (PAHs) during coking, and secondarily to the substances named in the previous paragraph.

The synthesis of this new pitch like product will be analyzed under a continuous process in a flow reactor.

2.5 Flow Reactor

Plug flow reactors are homogeneous chemical reactors that work in a steady state, that is, the properties of this type of reactors are constant over time. They are also known as PFR (Plug Flow Reactor) and are characterized by not axially mixing the streams that are inside the reactors and that are part of the process. In addition, this type of reactors can operate in different phases, whether liquid or gaseous, in which the composition of the fluid varies from one point through the direction of the flow of said fluid, assuming an ideal piston flow so that in this way the conversion is a function of position [37].

The plug flow reactor (PFR reactor) usually consists of an empty tube (hollow tube), it can also contain catalysts in package form to speed up or slow down the reactions that take place. The temperature and concentration profiles are expressed as a function of the position of the fluid within the reactor [38].

The reactants enter the reactor and flow through it in an axial direction. During the journey the reactants are consumed and the conversion increases with length. The operation of this type of reactor can be seen in the following Figure 9:

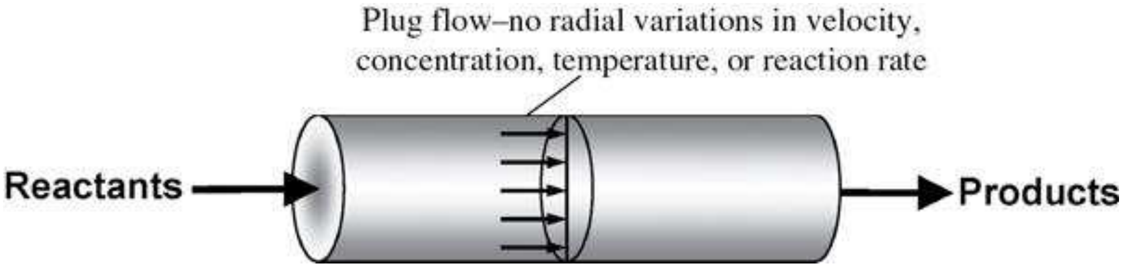


Figure 9 – Plug Flow Reactor, PFR [39]

Plug flow reactors (PFR reactors) are very similar to full mix reactors (CSTR reactors) in that they are both continuous flow reactors. These reactors differ in that they both have very different mixing characteristics.

2.5.1 Characteristics of a plug flow reactor

The most important characteristics of a PFR reactor (plug flow reactor) are the following:

- Continuous and not necessarily constant flow of the inlet and outlet currents (piston-type flow within the reactor).

- They work in a stable regime, so the characteristics do not change as a function of time in a given position.

- Absence of axial mixing inside the reactor.

- The mixing takes place completely in the radial direction inside the reactor. In this way, it is guaranteed that the properties of the fluid are constant in this plane.

- Density can vary according to flow direction.

- There may be heat transfer between the reactor and the surroundings.

- Chemical reactions take place in an open system.

- Pressure, temperature and composition vary in relation to the length of the reactor.

Taking these characteristics into account, we can establish that:

- Each of the elements of the fluid has a residence time within the reactor (tr), this time being the same for each of the elements. That is, this time is unique for all elements of the fluid and does not vary during operation.

- Flow properties can undergo continuous changes in flow direction.

- When each portion of the fluid is in the axial direction (regardless of its size) it acts as a closed system (it does not exchange matter with other portions that are ahead or behind) that is in motion.

- The volume of a fluid element is not necessarily constant throughout the reactor, and may experience changes in temperature, pressure and number of moles [40].

2.5.2 Plug flow reactor applications

Among the main applications of PFR reactors are the following:

- Widely used for reactive gas and vapor systems.

- They are ideal when a large production is required continuously.

- Frequently used for both exothermic and endothermic reactions.

- They can be used as fixed bed reactors, as long as they have catalyst-containing gaskets inside.

- Very popular for oil refining and butane, ethane and propane production.

- Widely used in different polymerization industries (ethylene), as well as food and beverage industries [41].

Its use, as in other reactors, has a series of advantages and disadvantages that we will describe below.

Advantage:

- They have a low operating cost, when compared to intermittent reactors.
- They work continuously.
- Automatic production control is very simple.
- They are very efficient.

Disadvantages:

- The initial cost is high.
- They are not the best choice for reactions with long residence times.
- The residence time is fixed for a given feed stream.

2.5.3 Material balance

To arrive at an equation that allows us to represent the composition of the reactants as a function of the distance within the PFR reactor (plug flow reactor), it is necessary to analyze the variation in the concentration of these reactants over time.

Previously, some assumptions must be taken into account, such as, for example, that the fluid is perfectly mixed in the radial direction and that as the reagent flow passes through the reactor, its concentration decreases. Likewise, it must be considered that there is no accumulation inside the reactor. Taking into account all these considerations, we will take the reactor as a system with continuous inlet and outlet flow to perform a mass balance, as we will see in the following Figure 10 [42]:

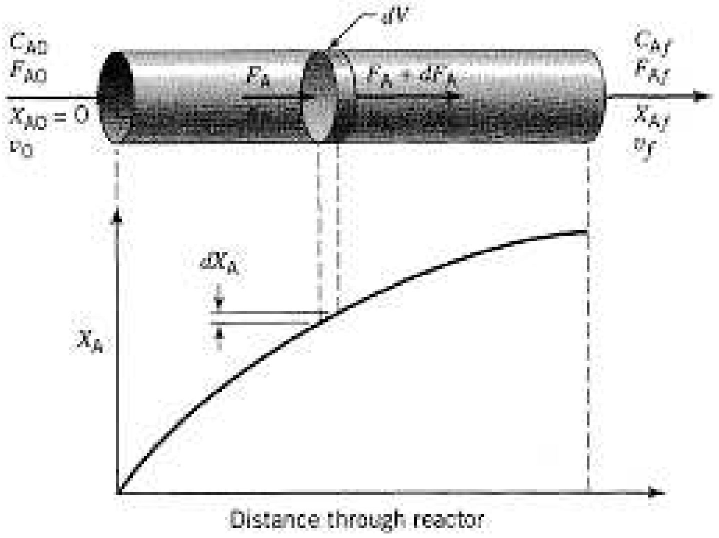


Figure 10 - Variables as a function of the distance from the reactor

When performing the mass balance, we arrive at the following expression:

$$\frac{dm}{dt} = m_{in} - m_{out} + reagent\ depletion$$

The first term represents the accumulation of mass, since there is no mass, it becomes zero, leaving the expression as follows:

$$m_{in} = m_{out} + reagent\ depletion$$

Substituting terms:

$$m_{in} = F_A$$
$$m_{out} = F_A + dFA$$
$$reagent\ depletion = -(r_A)dV$$

Regrouping and simplifying, we arrive at the following design equation for a plug flow reactor:

$$FA_0dX_A = -(r_A)dV$$

As in a CSTR reactor, the space time for a PFR reactor is defined by:

$$\tau = \frac{V}{v_0}$$

Where:

V: Volume of the tubular reactor.

v_0: Volumetric flow at the reactor inlet.

While the residence time can be deduced by the following expression:

$$dV = vdt$$

As described in the disadvantages of this type of flow reactor previously, it can be observed by means of the final equation obtained that the volume of the reactor will be directly proportional to the residence time, so it would not be suitable for this specific work. the use of this type of flow reactor, since a long-length reactor would have to be designed due to the relatively high residence time of the reactants during synthesis. The possible solution to this problem would be given by the use of a CSTR type reactor (Continuous Stirred Tank Reactor) [40].

2.6 CSTR (Continuous Stirred Tank Reactor)

Continuous stirred tank reactors (CSTR) are the most important process units in an industrial chemical process. In particular, the non-isothermal non-adiabatic CSTR is the reactor of greatest application for many reactions of industrial interest.

In the CSTR the reagents are introduced and the products are extracted simultaneously and continuously. A CSTR is generally considered to be homogeneous and is therefore modeled without spatial variations in concentration, temperature, or reaction rate throughout the vessel. In fact, the most important consideration in relation to the dynamics of the CSTR is that perfect mixing occurs within the reactor. This means that the properties of the reactant mixture are considered uniform anywhere within the reaction vessel and are therefore identical to the properties of the outlet stream [43]. Another important consideration is that the inlet stream mixes instantly with the mixture present in the reactor. In practice, if an incoming element of reactant material is evenly distributed throughout the tank in a much shorter time than the average residence time in the tank, then the tank can be considered well mixed. Figure 11 shows a general schematic of a CSTR.

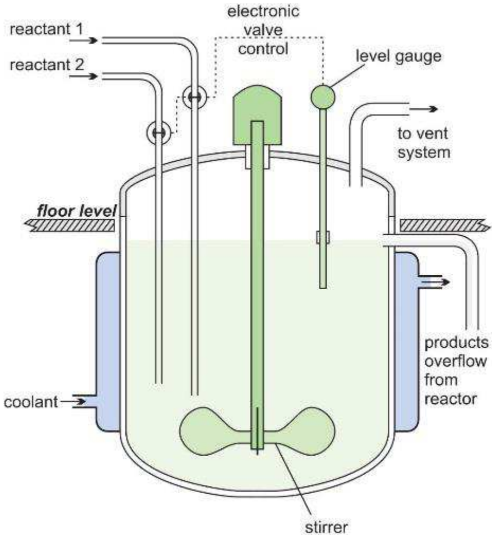


Figure 11 - Continuous Stirred Tank Reactor, CSTR [44]

Simple generic model of a CSTR There are complex interactions between transport phenomena and reaction kinetics that characterize CSTRs and determine their performance. The mathematical modeling of kinetic mechanisms and heat transfer phenomena has been an area of active research in chemical engineering in recent years. Unfortunately, in many cases the structure of the reaction kinetics remains uncertain. In a similar way to other articles on CSTR, this work uses a generic model where the chemical reaction A → B is carried out and a cooling jacket is used. The process variables are the reactant and product concentrations xA and xB respectively, the reactor temperature T, and the cooling jacket temperature Tj. When formulating the mass and energy balances, the following equations are obtained [42]:

$$\dot{x_A} = -k(T)x_A + d_r(x_A^{in} - x_A) \quad (1a)$$

$$\dot{x_B} = -k(T)x_A + d_r(x_B^{in} - x_B) \quad (1b)$$

$$\dot{T} = bk(T)x_A + \gamma_1(T_j - T) + d_r(T^{in} - T) \quad (1c)$$

$$\dot{T_j} = \gamma_2(T_j - T) + d_j(T^{in} - T) \quad (1d)$$

Where the kinetic constant is expressed according to the Arrhenius equation,

$$k(T) = k_0 exp\left(-\frac{E}{RT}\right)$$

The superscript in indicates the input conditions, γ1 and γ2 indicate the heat transfer parameters, b is the reaction enthalpy, and dr and dj are the dilution speed of the reactant mixture and of the cooling medium, respectively.

The first term to the right of Eq. (1c) in model (1) is the generation of heat by reaction, the second term is due to the cooling / heating of the reactant mixture by the cooling jacket, and the third Term is the total heat loss due to the flow of reactants and the output of products. The heat that is removed through the reactor wall is proportional to the area of the wall and the difference in temperature between the reactant mixture and a cooling medium circulating through the jacket. In practice, the heat extraction process is regulated by manipulating the speed of the cooling fluid. In many cases the dynamics of the jacket is fast compared to the dynamics of the reactor, and therefore the speed of the cooling fluid is linked to the temperature of the jacket. It is well known that the exponential dependence of the reaction rate on the reactor temperature is one of the main non-linearities of the CSTR. As a consequence of the non-linearity of the reaction kinetics, the CSTR can display a great variety of dynamic behaviors, from multiplicity of stationary states, sustained oscillations [45].

These reactors are based on the different kinetic parameters that depend on the reaction on which it is going to be studied, and they can be reactions of order 0, 1, 2, etc., as will be detailed below.

2.7 Reaction rate expressions

The speed or rate of a reaction corresponds to the speed with which a reactant (compound) disappears or the speed of formation of a product. For biological processes, the concept of the reaction rate is of interest both to define the kinetics of consumption of the substrate by microorganisms, and to follow their growth kinetics. The numerical value of the reaction rate (r) is defined as the amount (mass, moles) of material (reactant, compound) that reacts per unit volume and per unit time. Units of r are expressed, for example, in mg/L. h, as units of concentration over units of time.

However, the mathematical definition of (r) does not correspond to the popular expression r=dC/dt which does not make sense, but only as a notation. The reaction rate is a quantity that depends on the temperature and the concentrations. The expression for r is essentially an algebraic expression involving concentrations and not a differential equation. In reference to a reaction involving two reactants, the most common function of dependence of the reaction rate on the concentrations is given by:

$$-r_A = kC_A^{\alpha}C_B^{\beta}$$

k: kinetic constant.

C: Concentrations of the reactants (A, B) in the reactor.

α, β: Constants.

The constants α, β, are designated by their order. The reaction given in the example is of order α with respect to A, of order β with respect to B, etc. The global order of the reaction is given by the sum α + β. The reaction is classified as an elemental reaction when the orders α, β, etc., are exactly equal to the stoichiometric coefficients a, b, etc., [45].

2.7.1 Zero order kinetics

Zero-order reactions are those that proceed with a rate independent of the concentration of the reactants or (of the substrate).

If the kinetics is order 0, the expression of the reaction rate is given by:

$$-r_s = k$$

$-r_s$: [kg/m3.d]

k: [kg/m3.d]

2.7.2 Kinetics of order 1

First-order reactions are those that occur at a rate directly proportional to the concentration of the limiting reagent (substrate). For such kinetics, the expression of the reaction rate is given by:

$$-r_s = kS^1 = kS$$

$-r_s$: [kg/m3.d]

k: [d-1]

S: [kg/m3]

Most aerobic wastewater treatment processes are appropriately described by a kinetic relationship of order 1.

2.7.3 Kinetics of order 2

In second-order reactions, the limiting substrate (reactant) disappeared at a rate proportional to the square of its concentration. And it is written as:

$$-r_s = kS^2$$

$-r_s$: [kg/m3.d]

k: [m3/kg.d]

S: [kg/m3]

In addition, as already mentioned, there are types of simple reactions, with complex speed laws, however these are more frequent in catalytic reactions for liquids or gases. The same situation of complexity expressed in the reaction rate is found when an overall reaction is one of the multiple types [45].

In this type of binder-type pitches, in addition to knowing the physical characteristics and the amount of coking to be obtained, it is also necessary to know the characteristics that are chemically related to the composition of this type of pitches, such as substances insoluble in toluene (TI) and quinoline insoluble substances (QI).

2.8 Toluene insoluble substances (TI)

Toluene, as seen in Figure 12, is a chemical compound belonging to the group of aromatic hydrocarbons, its appearance is liquid at room temperature, colorless and insoluble in water. It is also known as methylbenzene and its main use is as a solvent for organic substances, its industrial use is high because it is a non-carcinogenic substance [46].

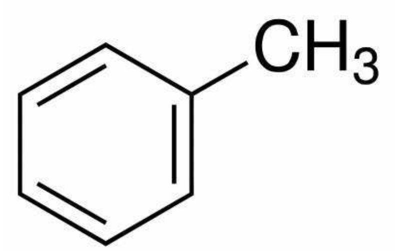


Figure 12 - Toluene, molecular structure

Specifically, in coal tar or in bituminous substances, substances insoluble in toluene are highly desired for the production of binding pitches with high coking values because they act as precursors of this substance, frequently given in the temperature range of 360 to 430 °C achieving a formation of the mesophase and later the formation of coke as seen in Figure 13 [47].

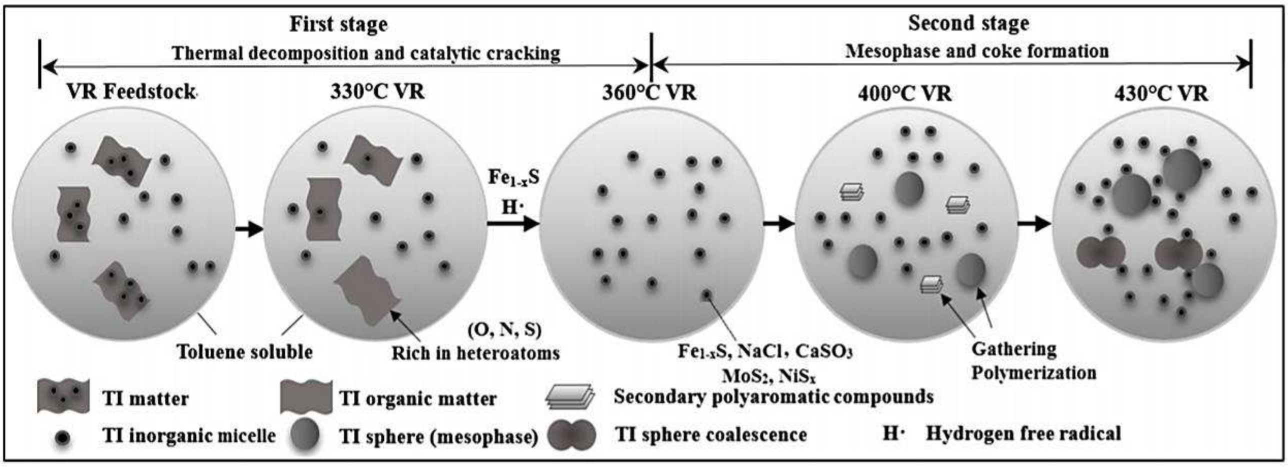


Figure 13 - Schematic of the TI evolution in CTVR (Coal Tar Vacuum Residue)

The content of insoluble in toluene is a parameter that is frequently used to determine the degree of polymerization achieved after treatments of precursors of carbon materials. Therefore, it is related to the molecular size of the compounds present, although other factors such as polarity may contribute at the same time.

It is frequently used for the measurement of possible selective interactions of the different reinforcements in the characterization of pitches. Toluene insoluble substances are intermediate molecular weight between quinoline insoluble substances and high boiling point oils [48].

2.9 Insoluble substances in Quinoline (QI)

Quinoline is a colorless liquid with a strong odor. It is a contaminant in some dispersing agents for colorants. Chemically it is a heterocyclic organic compound formed by the union of a nucleus derived from benzene and another pyridic; Furthermore, these compounds have an isomer called isoquinoline, its basic formula is C9H7N and its structure is shown in Figure 14 [49].

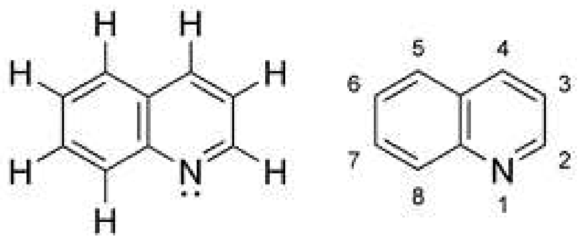


Figure 14 – Quinoline, chemical structure

QI materials consist of carbon, very high molecular weight materials, forming in the pitch and in the mesophase during heat treatment. The concentration of TI and QI is restricted due to their negative effects on the kinetics of mesophase formation, which results in a disruption of the graphitic structure during pitch carbonization [50].

Regarding the factors that affect the growth of the mesophase, Brooks and Taylor, found a marked association between QI particles and mesophase spheres during the early stages of mesophase formation and they also found that, in pitches containing abundant QI particles, the mesophase spheres were more numerous and smaller than in those with less insoluble or even absent. They also noted that QI particles predominantly reside around the surface of any mesophase sphere present and that in sufficient numbers, QI particles inhibit the regular growth of spheres and their coalescence [50].

Because the carbon structure is inherent to the mesophase precursor, the physical properties of the mesophase prepared carbons are significantly affected by the concentration and type of insolubles contained as shown schematically in Figure 15 [51].

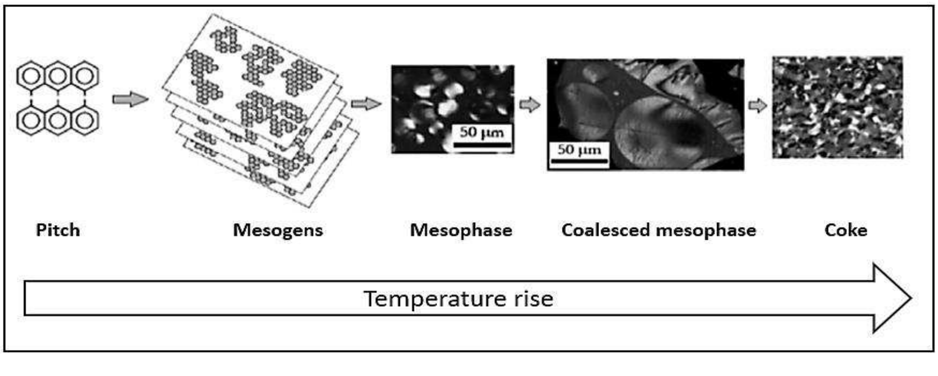


Figure 15 - Pitch coking mechanism

A distinctive characteristic of tar or bituminous substances compared to other types of tar is the existence of very small dispersed solid particles of approximately 1 um in diameter. These particles are called primary quinoline insoluble (QI) substances for the reason that they are insoluble in most solvents even as energetic as quinoline.

These substances are generated during the primary cracking processes that take place in the coking oven and are entrained by the gases to become part of the tar and later of the pitch. Its composition is based mainly on carbon and oxygen and its is highly influential on the physicochemical properties and the pyrolysis behavior of the pitches and their applications [52].

This type of substances insoluble in quinoline (QI) are highly desired in a binder-type area for the production of anodes, since they favor their binding effect in addition to influencing the increase in carbon yield. These types of substances can also be harmful when you want to give another type of use to the pitch, such as for the production of carbon fibers since they can cause morphological defects due to the fluidity of the pitch [52].

3 Experimental Methodology

The development of this part of the research is related to the basic objectives that have been defined above, including the determination of the most relevant physical and chemical properties in the process of obtaining a material called Pitch like product that will serve as a binder for the carbon anode producing industry to be used in the Hall-Héroult process to obtain metallic aluminum.

The resolution of this project is given by:

- Definition and resolution of a viscosity model based on the temperature that best suits the development of the process and the main characteristics of the raw material.

- Definition and resolution of a pressure model as a function of temperature that allows determining the final pressure conditions conditioned by the release of gases from the raw materials.

- Definition and resolution of a reaction kinetic model as a function of the temperature that best adapts to the majority compounds of matter and the type of reactions they generate during their heat treatment.
- Definition and resolution of the intrinsic characteristics of the final product such as the determination of the softening point, substances insoluble in toluene and substances insoluble in quinoline.
- Resolution of the mathematical models with MATLAB R2019a, to obtain the specific results at the final conditions of the process, as well as the figures of their variation as a function of temperature.

The definition-selection of each one of the mathematical models for the calculation of the respective properties, will be carried out based on the work of Safin, et al., with the topic “Co-processing of bituminous coal with a mixture of coal tar and heavy Residues Petroleum Derivatives”, in which a binder was experimentally synthesized using the following raw materials as compounds.

- Coal tar (CT): from the coking process provided by the Altai-Koks plant, they were used as paste-forming solvents.
- Coking coal: grade 1GZh from Chadansky deposit - Ulug-Khem coal basin.
- Product derived from petroleum: raw material for the production of grade "A" black coal, produced by the Omsk refinery.

These raw materials were mixed in equal parts to obtain a mass of 3 kg in the reactor under an inert atmosphere that is achieved with nitrogen gas.

Within the reactor, some options were evaluated to determine the best synthesis conditions, which were later to be evaluated by measuring their properties, softening point, coke value, substances insoluble in toluene and quinoline, benzo[a]pyrene content, by analytical methods using equipment and measurement techniques such as liquid chromatography or Fourier-transform infrared spectroscopy (FTIR).

The determination of the best synthesis conditions was based on the selection of 8 experiments in which the pressure, mass flow and temperature values were changed and combined. The temperature values to which the mixture was subjected correspond to 390, 420 and 450 °C, while the pressure values were given at 12, 14 and 16 atm. A basic diagram of the experimentation process is shown in Figure 16 below.

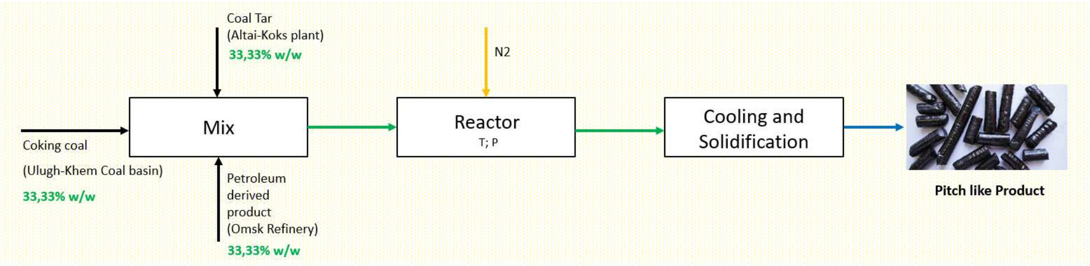


Figure 16 - Diagram of the experimentation sequence

Additionally, the amounts obtained from the gas phase resulting from the evaporation of volatile substances from the mixture during the process were measured. This can be better observed through the experimental scheme of Figure 17, where all the elements that intervene in the experimentation are represented, such as the nitrogen tank useful to maintain an oxygen-free atmosphere (1), the mixing pump of the raw materials (2) which is connected to the reactor with valves that allow the exit of both the product (4) as well as the volatile substances which are directed towards a cooler where they are separated into two phases, the condensable liquid phase (3) and gases that cannot be recovered or losses (5).

The value of these volatile condensable substances corresponded to a value of 5.5 to 22.2% w/w, while the non-condensable substances and losses of 6.8 to 14% w/w respectively.

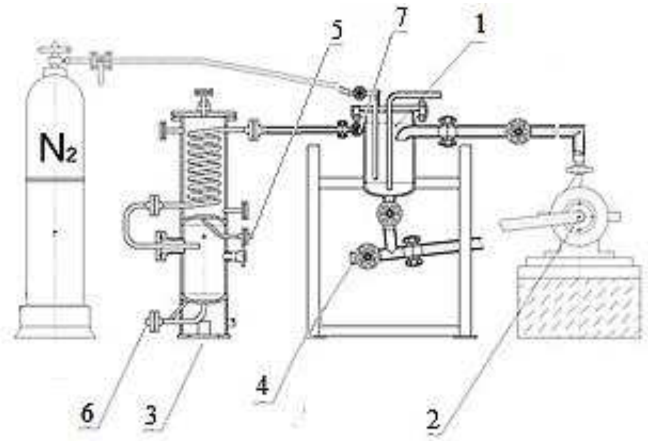


Figure 17 - Experimental scheme in obtaining the Pitch like product

Based on these experiments, a resolution of the mathematical models will be executed taking into account physical-chemical properties of compounds that most closely resemble those of the raw materials used, so that in this way it can serve as a point of comparison in the determination and in the analysis of the results.

3.1 Definition and resolution of a viscosity model as a function of temperature

The kinematic and dynamic viscosity values were evaluated to obtain a useful characteristic for the handling and transport of the final product. For the calculation of the kinematic viscosity, three mathematical models were used, which are detailed below:

- Model of Moharam et al.

Whose equation as a function of temperature corresponds to:

$$ln[v(10^{-6})] = A\, exp\left[\left(\frac{T_b}{T}\right)(SG)^{B}\right] + C$$

Where:

v: Kinematic viscosity

T_b: boiling point

SG: Specific Gravity

While the values A, B and C represent constant, empirical values, characteristic of this model, their value is given by the following expressions:

$$A = 1.0185$$

$$B = \frac{T_b}{305.078}$$

$$C = -3.2421$$

- Mehrotra model [46]

It is represented by the following equation:

$$\log\log[v(10^{-6}) + 0.8] = a_1 + a_2\, log(T)$$

Again, the values of a_1 and a_2 represent empirical values, represented as follows:

$$a_1 = 5.489 + 0.148(T_b)^{0.5}$$
$$a_2 = -3.7$$

Where T_b is equivalent to the boiling point value of the mix.

- Aboul-Seoud and Moharam model

For this equation, the previous models are taken as a basis with a slight correction in the constant a_1, which will now also be influenced by specific gravity, as will be seen below:

$$\ln\ln[v(10^{-6}) + 0.8] = a_1 + a_2\, ln(T)$$

$$a_1 = 4.3414(T_bSG)^{0.2} + 6.6913$$

$$a_2 = -3.7$$

The three models defined above can act in a wide range of temperatures, specifically from 323 to 823 K and were evaluated in the work of Tovar, et al., where very good results were achieved, reaching up to 2.54%. error with respect to the experimental results.

The models for the calculation of dynamic viscosity correspond to the models in which the lowest percentage of error was obtained in the work carried out by Bahadori, et al., in which he analyzes 8 experimental calculation models and even proposes his own model with its own parameters:

- Hossain Model

$$\mu = 10^{(-0.71523*API+22.13766)}T^{(0.269024*API-8.26)}$$

- Bahadori-Mahmoudi-Nouri model

$$ln(\eta) = a + \frac{b}{CAPI} + \frac{c}{(CAPI)^2} + \frac{d}{(CAPI)^3}$$

Where:

a, b, c: Correlating parameter in the viscosity correlation

$CAPI$: Correlating parameter defined by the following relation

$$CAPI = API\left(\frac{Sa}{Ar + Re + As}\right)$$

Sa: Saturated hydrocarbons

Ar: Aromatic hydrocarbons

Re: Resins

As: Asphaltenes

The values are given in mass fraction.

- Cornelissen-Waterman Model

This equation has been widely used for the determination of highly viscous substances originally used for the determination of viscosity in heavy petroleum products, however its use has been extended to other substances with similar behavior such as coal tar. Its Equation is defined by [53]:

$$\log \eta = AT^{-5} + B$$

The units used in this equation correspond to the absolute scale in kelvins for temperature and in centipoises for the viscosity value.

The values of A and B are empirical constant values that depend on the temperature range in which the process is carried out, the authors give a large number of values of these constants for the most approximate determination of the viscosity of the mixture.

3.2 Definition and resolution of a vapor pressure model as a function of temperature

As previously detailed, despite the fact that they are highly viscous substances with high heavy components whose boiling point corresponds to temperatures above 600 ° C, these substances also have volatile compounds that will contribute to the increase in pressure within the reactor. One of the substances that most affects the increase in this property corresponds to the petroleum-derived product, it has volatile substances that are detachable at the temperatures under which the process occurs [54].

For the evaluation of this property, there are not many models that can be coupled to the type of raw materials with which we are working in this project, however, there are two important relationships that are widely used and that according to their authors have produced results that are very similar to results that can be obtained when conducting experiments on either a laboratory or industrial scale.

- Riazi model

$$log_{10}\left(1x10^5 P_{vap}\right) = 3{,}2041\left[1 - 0{,}998\left(\frac{T_b - 41}{T - 41}\right)\left(\frac{1393 - T}{1393 - T_b}\right)\right]$$

This equation is suitable for bituminous substances in general, but produces more accurate results with high-boiling-point oil fractions. Its input variables correspond only to the boiling point temperature and the temperature at which you want to calculate the vapor pressure [55].

- Fletcher model

It is based on the Clapeyron-Clausius equation determined as a function of temperature, and is given by the following expression [56]:

$$P = \alpha \times exp\left(\frac{-\beta \times M^{\gamma}}{T}\right)$$

Where:

P = [atm]

T = [K]

M = Average molecular weight, value in the range 190 to 450

α = 87060

β = 299

γ = 0.59

This last model is more related to the vapor pressure emitted by substances such as coal tar or products with similar characteristics.

3.3 Definition and resolution of a reaction kinetic model as a function of temperature

By increasing the temperature of bituminous compounds as explained above, a series of thermal cracking reactions take place, reactions in which coke is formed. Although these compounds exist, they are made up of hundreds of chemical substances, the molecular groups that affect almost all of their formation correspond to groups of olefins, dienes and aromatics. Therefore, the equations to be solved are given in reference to the amount of these compounds in our raw materials, using as a mathematical model the one developed in the work of Towfighi [50].

- Towfighi, et al., model

The determination of the equations that govern the formation of coke were obtained from the reaction mechanism and kinetics, taking into account the aforementioned compounds, obtaining the following relationships:

$$R_{olefin} = k_{01} e^{\left(-\frac{E_1}{RT}\right)} \left(k_{C_2H_4} * C_{C_2H_4} + k_{C_3H_6} * C_{C_3H_6}\right)$$

$$R_{diene} = k_{02} e^{\left(-\frac{E_2}{RT}\right)} C_{C_4H_6}$$

$$R_{aromatic} = k_{03} e^{\left(-\frac{E_3}{RT}\right)} \left(k_{C_BH_B} * C_{C_TH_T} + k_{C_XH_X} * C_{C_SH_S}\right)$$

R_i corresponds to the final value of the coke that will depend on the temperature value. The author of these equations mentions that the compounds being part of the same group have the same activation energy, so it can be taken as a constant of the process which is provided by obtaining its value from experimental data, in the same way with the determination of the kinetic constant that will condition the amount of coke to be obtained. The value of these constants is shown in Table 2.

Table 2 - Kinetic parameters of coking model

Group	$k_0 \left[\frac{Kg\ coke}{m^2 * hr * \left(\frac{kmol}{m^3}\right)^3}\right]$	E $\left[\frac{J}{mol}\right]$	R $\left[\frac{J}{mol * K}\right]$
Olefins	7,8589x10^8	7,4164x10^4	8,3143
Butadiene	2,099x10^12	1,6240x10^4	
Aromatics	4,1865x10^8	2,9977x10^4	

3.4 Definition and resolution of the intrinsic characteristics of the final product

These characteristics will correspond to the values of the softening point, substances insoluble in toluene and substances insoluble in quinoline, whose mathematical relationships will be explained separately:

3.4.1 Softening Point (Sw)

The determination of this value is related to the characteristics of each compound, among which is considered the boiling point temperature, chemical composition, among others. This value, in addition to being able to be measured experimentally with the ball and ring test, as explained previously with the ASTMD 36-95 standard, can also be determined indirectly with results very similar to the experimental ones, taking into account the characteristics used. in the determination of the viscosity of Cornelissen & Waterman that proposes an equation involving its empirical constants A and B, as shown below:

$$A = (0.358\, S_w + 4{,}82) \times 10^{12}$$

The value of the softening point (Sw) will be given in degrees centigrade.

3.4.2 Substances insoluble in toluene (TI)

This value, which is usually determined by experimental measurement methods such as the use of gas chromatography, however can also be determined by approximate means based on the constants previously defined in the work of Cornelissen & Waterman.

$$B = 0{,}0191\, I - 0{,}318$$

Another model that can estimate the value of this type of substances corresponds to that of the work carried out by Shoko, et al., [51].

- Shoko, et al., model

$$\mathrm{TI} = -40051{,}28 + (0{,}56 * \mathrm{CV}) + (0{,}07 * \mathrm{FC}) - (2{,}4 * \mathrm{moisture}) + (10{,}63 * \mathrm{ash}) + (400{,}53 * \mathrm{C}) + (393{,}74 * \mathrm{H}) + (439{,}21 * \mathrm{N}) + (348{,}39 * \mathrm{S}) + (399{,}19 * \mathrm{O})$$

Where C, H, N, S, O correspond to the corresponding amount of carbon, hydrogen, nitrogen, sulfur, oxygen found in the final product:

CV: Coking value

FC: Fixed carbon

3.4.3 Substances insoluble in Quinoline (QI)

Its determination can also be obtained based on the work of Shoko, et al., In which, in addition to the characteristic chemical properties, the value of the softening point (SP) and the content of volatile substances (vol) are taken into consideration. as expressed below.

$$QI = 161{,}71 - (0{,}12 * \mathrm{SP}) + (0{,}40 * \mathrm{CV}) - (3{,}10 * \mathrm{FC}) - (11{,}42 * \mathrm{ash}) \\ - (3{,}04 * \mathrm{vol}) + (1{,}70 * \mathrm{C}) - (15{,}93 * \mathrm{N}) + (3{,}00 * \mathrm{O})$$

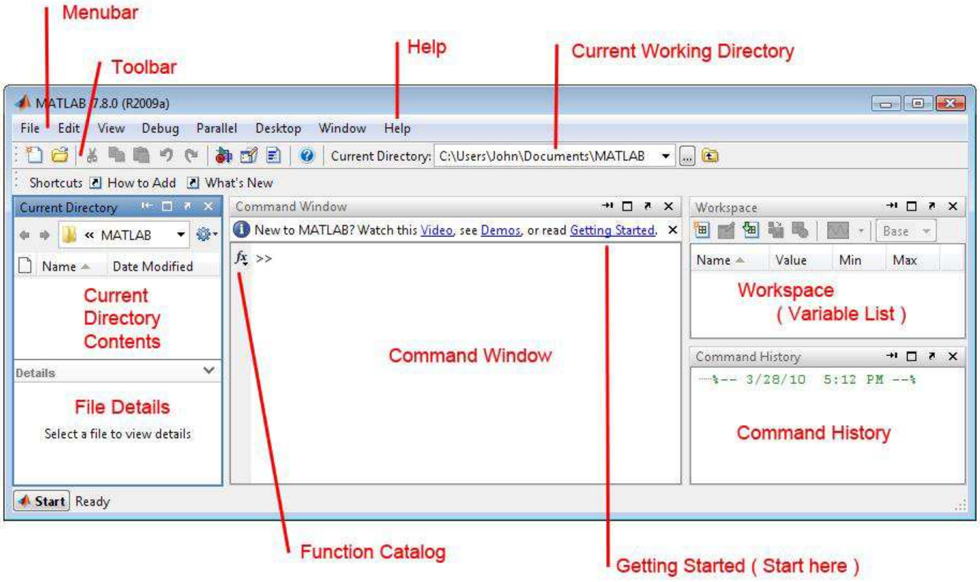
For the resolution of all mathematical models, MATLAB R2019a has been proposed as software for calculating and simulating the different variables involved in the process up to a maximum temperature of 420 C.

3.5 Resolution of mathematical models with MATLAB R2019a

The use of this software has been preferred because over time MATLAB has evolved into a basic instructional material, both for applied mathematics courses and for very advanced courses in other areas. In industrial settings it is used for research and solving practical problems and engineering calculations. Typical applications of MATLAB are numerical calculus, algorithms, problem solving with matrix formulation, statistics, optimization, and so on many other applications in the context of mathematics, and how not to highlight the MATLAB Software for the application in the study, simulation and design of dynamic and control systems.

MATLAB (Matrix Laboratory) is a high-level language, designed to provide facilities for numerical calculations, visualization and programming in a very easy-to-use environment. MATLAB offers a very versatile integrated development environment (IDE) with its own programming language (M language). Provides an interface with 64 command lines to solve linear and nonlinear problems, as well as other experiments in numerical form. Use simple mathematical notation to treat and solve problems. Its power lies in the efficient handling of matrices, it also includes its own compiler which allows to extend its use allowing the user to create their own commands, classes and functions.

MATLAB's capabilities can be extended with toolboxes. Thus, for example, toolboxes for Mathematics and Optimization, Statistics and Data Analysis, Design of control and analysis systems, Signal and communications processing, Image processing, Tests and measurements, Computational biology, Artificial Neural Networks, Modeling can be used. and financial analysis, development of applications or reports and connection to databases, which facilitates the study of dynamic systems and their regulation. It is compatible with one of the most used programming languages: C and Fortran, as well as easy compatibility with Microsoft Excel where the results can be directly exported for a better presentation and design types, making it a very versatile program in its use [57]. A screenshot of the workspace and its components is shown in Figure 18.



New to MATLAB? Watch this Video, see Demos, or read Getting Started.

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Figure 18 - MATLAB work environment

4 Results

The results will follow the order set out in the methodology. In which the values obtained through the MATLAB R2019a programming code presented in appendices A, B, C and D will consist, in addition to the results of the figures during the analysis range.

For the subsequent analysis of results, all the values expressed in this section will correspond to the results obtained with the properties of the sample under which the best results were obtained during experimentation. That is, setting the analysis range with initial conditions of pressure and temperature of 1 atm and 25 °C to the edge or final conditions of 16 atm and 420 °C.

4.1 Viscosity as a function of Temperature

The results obtained correspond to the resolution of the Cornelissen-Waterman model, for reasons that are explained later in the discussion of results, obtaining the values tabulated in Table 3.

Table 3 - Viscosity values at different temperatures of the pitch like product

Temperature [°C]	Viscosity [Poises]
25	-4,2508e+04
40	2,4406e+05
80	5,0524e+03
120	48,4243
160	2,6766
200	0,8049
240	0,0973
280	0,0376
320	0,0013
360	3,1055e-04
400	7,9188e-05
420	3,5146e-05

Representing these values in a Viscosity vs Temperature graph, the following trend is obtained, shown in Figure 19,

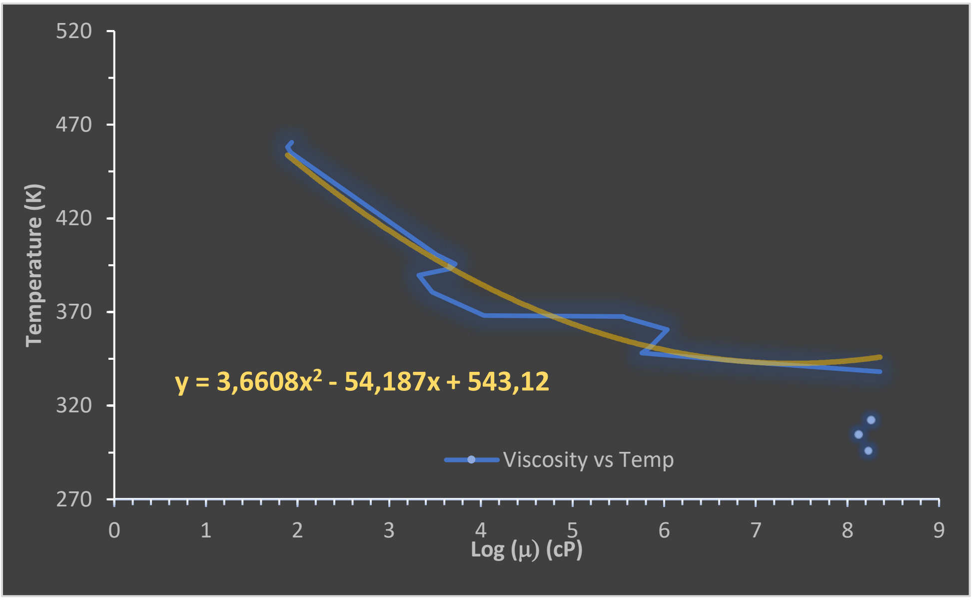

Figure 19 - Viscosity vs Temperature of the pitch like product

4.2 Total pressure of the reactor as a function of temperature

The values of the total pressure inside the reactor are presented in Table 4. Which is given by the sum of the partial pressures of the petroleum derived product and the coal tar, obtained under the Riazi and Fletcher models respectively.

Table 4 – Total pressure values at different temperatures

Temperature [°C]	P (atm)
25	-2,79
40	-2,05
80	-0,11
120	1,84
160	3,79
200	5,73

Continuation of Table 4

Temperature [°C]	P (atm)
240	7,68
280	9,63
320	11,57
360	13,52
400	15,47
420	16,44

In order to better observe the effect of each component at total pressure, the trend of its values is represented in Figures 20 and 21.

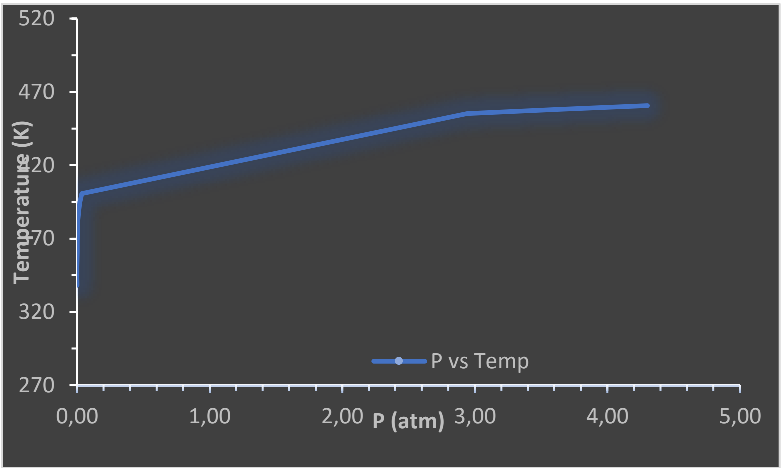

Figure 20 – Petroleum derived product Pressure vs Pitch like product Temperature

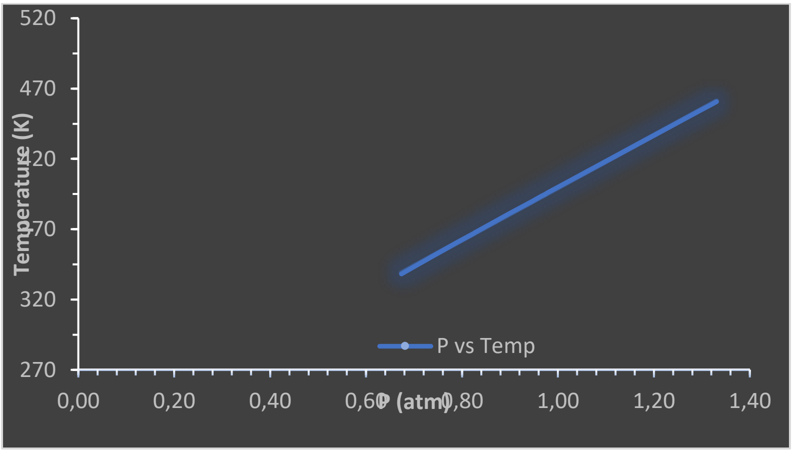

Figure 21 – Coal Tar Pressure vs Pitch like product Temperature

Obtaining in Figure 22 the total pressure trend as a function of the increase in temperature as the contribution of both partial pressures.

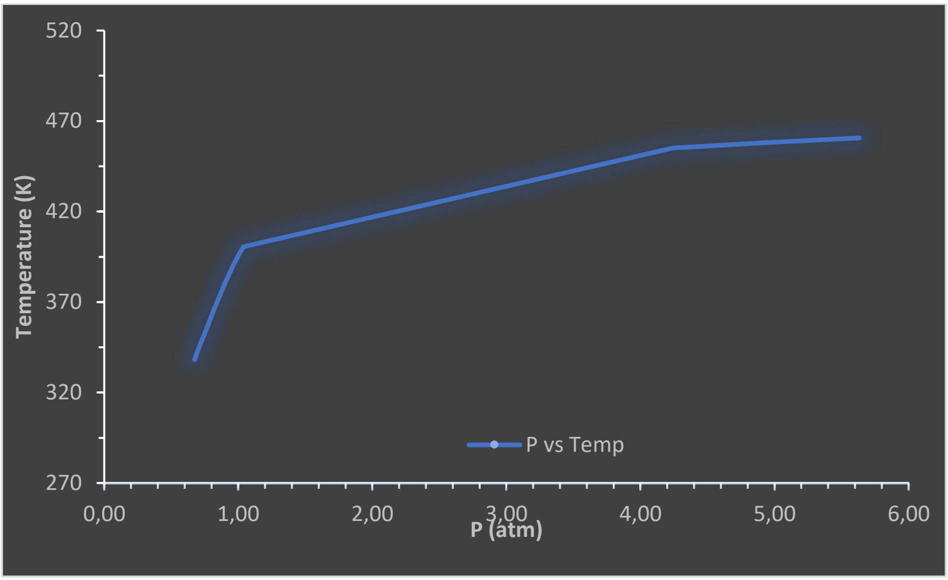

Figure 22 - Total Pressure vs Pitch like product Temperature

4.3 Coke formation as a function of temperature

The formation of the coke or carbon in suspension, is given by the sum of the values contained in the coal tar, coking coal and that formed from the petroleum derived product, obtaining, in Table 5, the following results in percentage by weight with Regarding the final product, pitch like product.

Table 5 - Coke formation values at a defined temperature

T [(°C]	Coke value [%]
25	44,1652
40	44,4971
80	45,3099
120	46,0354
160	46,6906

Continuation of Table 5

200	47,2878
240	47,8365
280	48,3441
320	48,8161
360	49,2574
400	49,6716
420	49,8696

The values that correspond to this table are represented in Figure 23.

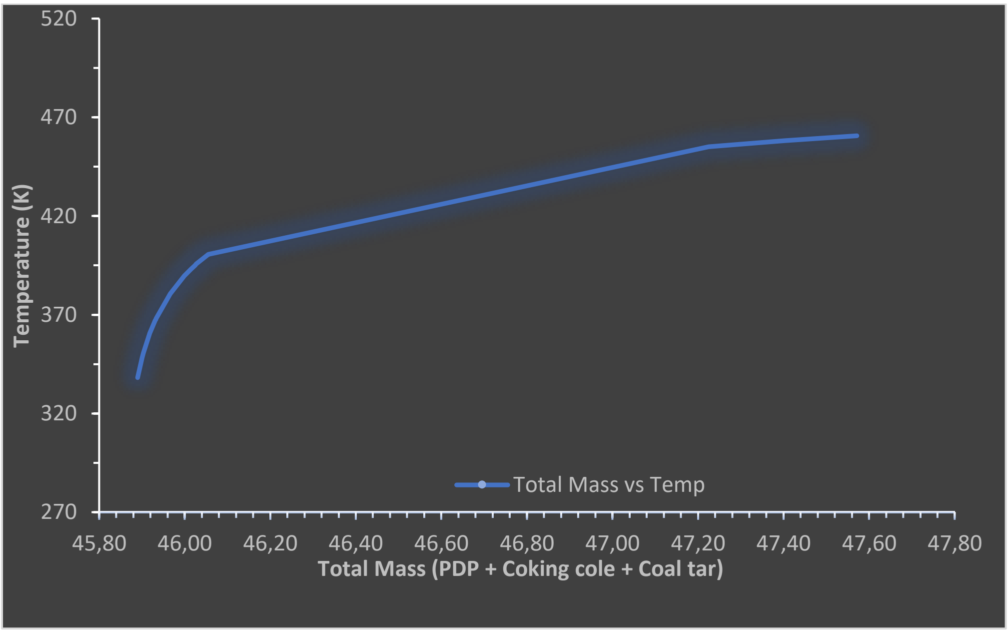

Figure 23 - Total coke formation in the pitch like product vs Temperature

While the coke formation values from the dienes, aromatics and olefins groups of the mixture are represented respectively in Figures 24, 25, 26.

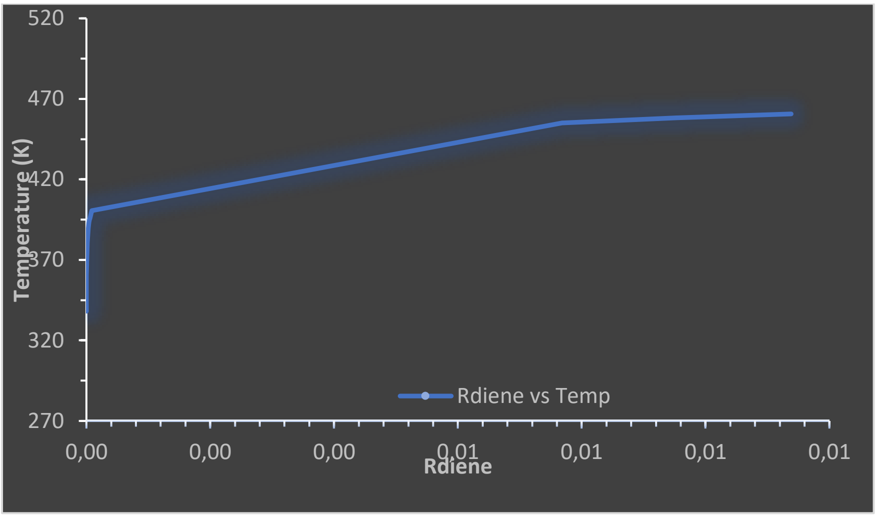

Figure 24 - Coke formation from dienes vs Temperature

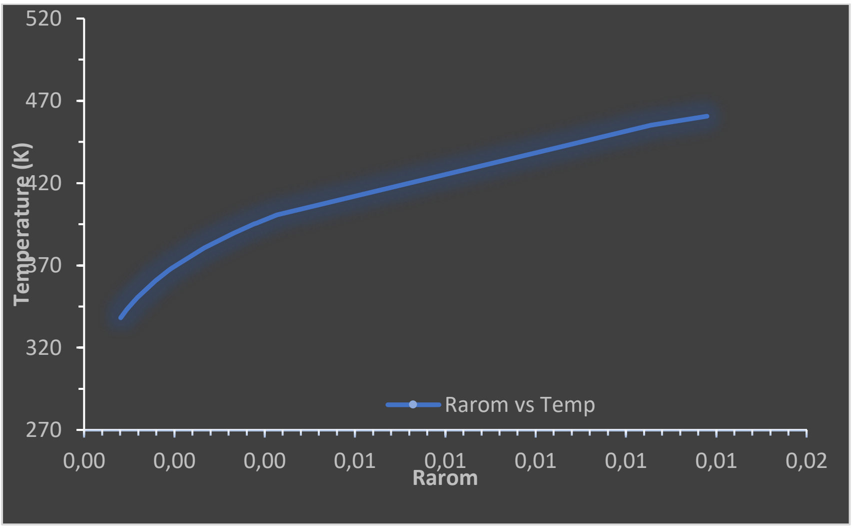

Figure 25 - Coke formation from aromatics vs Temperature

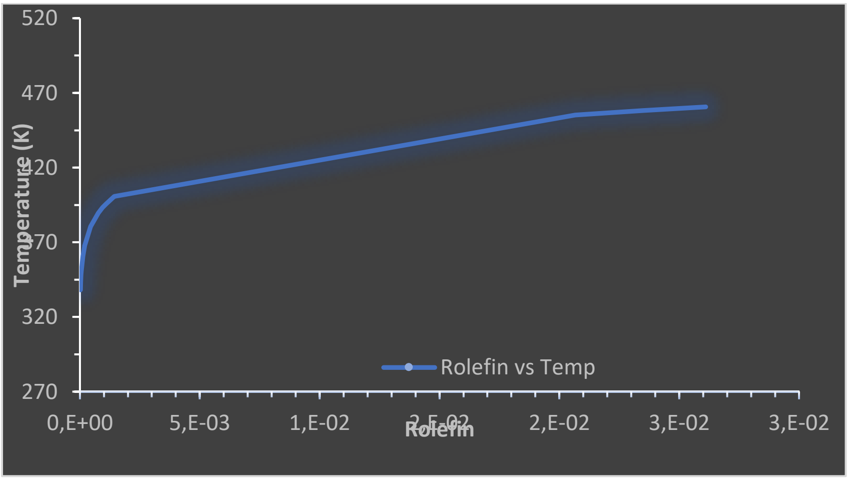

Figure 26 - Coke formation from olefins vs Temperature

4.4 Determination of the Softening Point

The value of the softening point of the final product, pitch like product, corresponds to 114.1899 °C. This value is not related to the temperature range in which the process was carried out, so it is defined as an intrinsic characteristic of the product. This value was calculated based on the methodology through an iteration of the constant B.

4.5 Determination of substances insoluble in toluene (TI)

The value of the substances insoluble in toluene calculated using this model corresponds to 31,6021% using the Cornelissen & Waterman model. While using the model of Shoko, et al., The result obtained was 29,3912% taking into account the elemental chemical composition and the amount of moisture, ash, coking value, fixed carbon estimated in the final product.

4.6 Determination of substances insoluble in quinoline (QI)

The value of quinoline insoluble substances calculated using this model corresponds to 6,5187 %. This was carried out following the parameters made in the calculation of substances insoluble in toluene, in which, in addition to the elemental chemical composition, the softening point and volatile matter values were considered.

4.7 Schematic representation of the process

This basic representation includes from the entrance of the raw materials to the mixer to the exit of the product and the gases generated during the process to the cooler.

Its representation has been made with the use of AutoCAD Plant software in 2D and 3D corresponding to Figures 27 and 28 below:

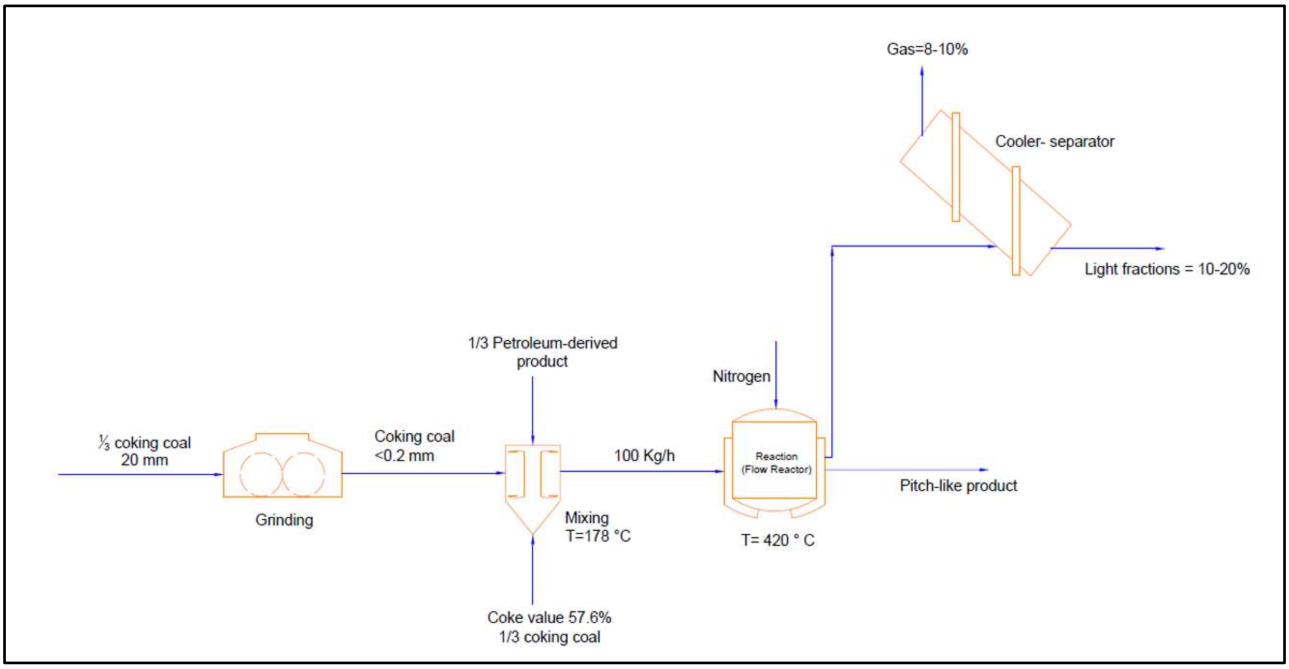

Figure 27 - Scheme of the process in the production of the pitch like product, AutoCAD Plant 2D

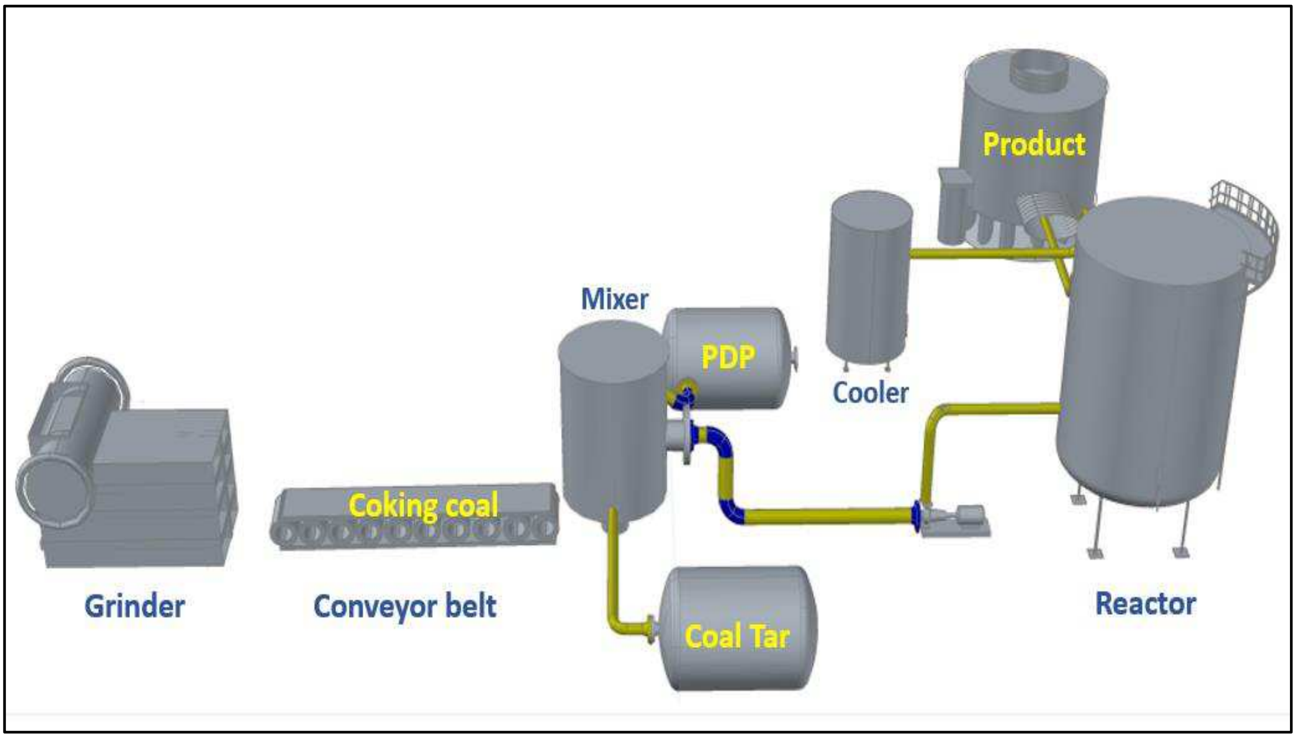

Figure 28 - Scheme of the process in the production of the pitch like product, AutoCAD Plant 3D

5 Discussion of Results

The discussion of the results is based on the analysis of the applicability of the results. This is done by comparing the data obtained in the simulation with the results obtained through experimentation in the laboratory, which has been detailed in the methodology. In addition to the use of complementary data obtained from bibliographic sources for a broader comparison in the validation of these results.

The results that have been shown in this work correspond only to those obtained by the models that best adapted to the raw materials taken as reference, chosen due to the great similarity with the raw materials that were used in the work of Safin, et al. The models that did not adapt to these conditions were excluded for a better practicality of this investigation.

5.1 Analysis of the change in viscosity as a function of temperature

Regarding the determination of the viscosity, it has been preferred to present the results of the dynamic viscosity above the kinematic viscosity since in addition to resulting in more precise values according to experimental reference data, this property is closely related to the nature of the substance and is highly dependent on the temperature at which the process is carried out.

The Bahadori-Mahmoudi-Nouri model allowed to obtain viscosity values close to those obtained in bibliographic data due to a very good adjustment of parameters that are carried out in obtaining this equation in which they eliminate the dependence of this variable with respect to pressure obtaining an equation dependent only on parameters that can be determined in a typical characterization of oil, such as through SARA analysis, however the resolution of this equation is only limited to calculating viscosity values corresponding to a temperature below The 177 °C, higher temperature values result in wrong viscosity values that do not correspond to this type of compound, thus being applicable only up to the preheating process of the raw materials just before being sent to the reactor, so it does not correspond to a scalable model for the entire synthesis process or at least for the vast majority.

The Hossain model turned out to be a very good option for calculating viscosity, especially for temperature values above the range used in the previous Bahadori-Mahmoudi-Nouri model, resulting in increasingly precise viscosity values. by increasing the temperature of the mixture compared to experimental values in the literature and also with the advantage of requiring only the API value of the mixture. However, in the presentation of the results, those obtained through the resolution of the Cornelissen-Waterman model were preferred for two important reasons, the first because when using this model there was less dispersion in the viscosity value in the temperature range under which its determination is considered adequate and second, that this model is closely related to the calculation of the softening point and the substances insoluble in toluene that were subsequently calculated. This relationship occurs due to an excellent determination of the constants A and B which, in addition to being influenced by the characteristics inherent to the mixture, largely depend on the temperature range in which the operation is carried out.

The behavior of its trend in the Viscosity vs Pitch Temperature curve as a product of Figure 19 is expected for this variable, obtaining a decrease in its logarithmic value as the process temperature increases. This result is more evident and more practical when observing the results of Table 3 in which a lower value of viscosity corresponds to a higher temperature value, due to the cracking processes that are generated, breaking the molecular bonds of the higher molecules. length, causing a greater fluidity of the mixture. For this calculation of the viscosity, temperature values of up to 300 °C are recommended, although mathematically acceptable values are obtained up to even temperatures of 400 °C, these would not represent the mixture since its characterization by the formation of gas is extremely complex. caused by the most volatile substances in the mixture.

Similarly, observing the data in Table 3, the viscosity value corresponding to a temperature of 25 C is negative, which is not a valid result, since at this temperature the pitch like product is considered as a solid material.

These viscosity values, having a wide margin of error, even between experimental results, were compared with results obtained from bibliographic sources such as in the work of Woodrow, et al., In which it presents viscosity values versus temperature for a modified carbon binder material. Obtaining, at the value of 40 °C, an interval of values between 10^5 and 10^6 Poises, so the value of 2,44x10^5 fits perfectly within the characteristic range for this type of binders.

5.2 Analysis of pressure change as a function of temperature

With respect to the total pressure that would be obtained until reaching the process temperature, 420 °C, and according to the results obtained in Figure 22, an adequate tendency of the pressure increase can be seen when the temperature value increases, due to greater evaporation of its components as a result of the increase in its kinetic energy. Its value is made up of the contribution of the partial pressures of the Petroleum derived product and Coal tar, neglecting the value obtained from the coking coal due to its negligible contribution.

Figure 22 also shows that there is a relatively accelerated pressure increase in the corresponding initial temperature range up to an approximate value of 130 °C, which is related to the evaporation of water as a result of humidity and the lighter components of the respective raw materials, being more evident in the Petroleum derived product represented in Figure 20 compared to the behavior of the curve in Figure 21 corresponding to Coal tar, with a much more linear and slow increase due to its high content of substances. heavy, low volatility.

With respect to the results shown in Table 4, negative pressure values are observed at temperature values of 40 and 80 °C, the practical explanation of which lies in the fact that there is no pressure contribution from the raw materials due to the absence of evaporation in this temperature range.

When analyzing the representativeness of the results, these are evaluated based on those obtained in the experimental work of Safin, et al., Where the reactor is kept at a temperature of 16 atm at a temperature of 420 °C controlled by a valve. that allows the escape of gases, while inferring higher pressures that are adequately represented by the model proposed in this work, with a value of 16,44 atm, equivalent to 2,75% above that required by the process at the temperature of 420 °C.

5.3 Analysis of coke formation as a function of temperature

For the determination of the amount of coke formed (microcarbon), the proposed model adequately represented the process in comparison with experimental results, obtaining a final amount of 49,87 % with respect to the 49,5 % of the experimental one, a value higher by 0,75 % than it can be attributed to a possible not so exact measurement during the experimental characterization, however these results turn out to be identical for practical purposes.

To evaluate the formation of coke, this would correspond to a kinetics of order 1 due to the superscript used in the equations of the Towfighi, et al. Model, which greatly simplifies its study by considering groups of reacting compounds instead of individual compounds separately.

Table 5 shows that the formation of coke, during the temperature range of 200 to 420 °C is equivalent to a total value of 2,58%, which is a predicted value for both this temperature range and for the composition of the Petroleum derived product used, since the processes in which high amounts of coke formation are required are generally carried out at temperatures above 500 °C, as is the case of the Delayed Coking process that uses an average temperature of 560 °C. This coke value is also beneficial for the quality of the pitch like product, since a high content of coke will affect the mechanical characteristics of the anodes in their subsequent production.

It was assumed for this case that there is a negligible formation of coke from coal tar and coking coal since their coking temperatures are above 700 °C, so their values are added to the final percentage by means of a balance of mass as there is no change during the process.

5.4 Analysis of the softening point parameters, substances insoluble in toluene (TI) and substances insoluble in quinoline (QI)

Regarding the determination of the softening point, a value of 114,19 °C was obtained as a result, which falls within the recommended range of this variable, between 100 and 120 °C. It would be recommended as a continuation of this work to evaluate the heating effect of the mixture. to obtain the final product since, for example, by slowly increasing the temperature of the mixture, it can more efficiently get rid of the more volatile compounds that have softening characteristics in the product, so longer heating times could lead to obtaining a binder with a slightly higher softening point value. High softening point values (preferably not greater than 140 °C) are preferred in the industry as they are related to a better behavior against heat treatment, corresponding to high conductivity values, as well as having low resistivity values that are very convenient for the subsequent process. of electrolysis to which the cathodes made with this type of binder will be subjected.

In the calculation of substances insoluble in toluene (TI), the two models presented gave values that resemble experimental results. The TI of the experimental result corresponds to a value in the range of 26,9 to 41,1%, while with the application of the Cornelissen & Waterman model, a result of 31,6% and a value of 29,39% were obtained when using the model of Shoko, et al., with a difference of 2,21% between them, relatively high values that are considered of good quality in the production of anodes since these are the ones that provide a high binding capacity between the carbon particles. The same concept is applicable for quinoline insoluble substances, which obtained a value of 6,52% within the range of 5 to 10% demanded by this type of binders.

CONCLUSION

It was possible to simulate with the use of MATLAB R2019a a representation of the most important physical-chemical properties, such as viscosity, pressure, coke formation, softening point and substances insoluble in toluene and quinoline, whose range of values coincide with those that can be obtained experimentally or from tabulated data in bibliographic information sources.

A highly versatile ".m" file code was obtained, being able to achieve new characterizations of pitches, with a high degree of reliability, with only the change of the value of the characteristic variables of their raw materials. In this way, the best conditions of the process can be designed to obtain a product with the best possible quality.

It was possible to represent the viscosity equation, from the temperature of 40 °C with a value of 2,44x10^5 Poises to 300 °C above which its application is not recommended due to the interference produced by the changes of state.

A final pressure equivalent to 16,44 atm was obtained at a temperature of 420 °C, in which the partial pressure of the petroleum derived product is the one that contributes the most to the total pressure compared to what the coal tar can contribute as it is made up of less volatile components.

A total coke content of 49,67 % was obtained, which is conditioned by the kinetic constants of the reactions, but which is representative of this type of pitches.

It was possible to determine indirect values inherent to the product with high precision, such as; the softening point with a temperature of 114,19 °C, substances insoluble in toluene (31,6 %) and substances insoluble in quinoline (6,52 %).

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APPENDIX A

Code in “m” language from MATLAB software for the calculation of viscosity as a function of temperature

```
%% Viscosity vs Temperature
%define constants

A=[11.77 12.28 16.16 17.38 22.55 23.01 24.49 26.03 27 29.07 33.67 35.02 ...
   34.7 35.58 35.87 37.24 37.78 39.89];
A1=A*10^12;

% B=[-0.762 0.395 0.597 -2.117 -2.557 2.595 -2.339 0.872 -0.145 -1.871 ...
%     0.52 -1.911 -0.2 0.185 -0.899 0.715 5.693 4.386];

B=[-5.693e1 -4.386e1 -2.595e1 -2.557e1 -2.339e1 -2.117e1 -1.911e1 -1.871 ...
   -0.899 -0.872 -0.762 -0.715 -0.597 -0.52 -0.395 -0.2 -0.185 -0.145];
B1=-B/10;

Temprange1=[0 130; 5 135; 30 120; 5 120; 25 150; 30 158; 25 160; 10 180; ...
         35 180; 55 178; 45 195; 45 199; 40 200; 45 200; 55 200; 140 224; ...
         90 224; 130 245];
      %Temprange1 is in Â°C
Temprange=Temprange1+273.15; %define Temp in K
Timp=zeros(1,18);

%define Tavg for each constant
for i=1:18
  Timp(i)=((Temprange(i,2)-Temprange(i,1))/2)+Temprange(i,1);
end
Timp(1,4)=350.65; Timp(1,7)=367.65; Timp(1,13)=395.15; Timp(1,17)=458.15;
Timpprime=Timp';
Timpprimecelcius=Timpprime-273.15;
A1prime=A1';
B1prime=B1';

%define viscosity equation
   % log(n)=AT^-5 + B
n=10.^((A1prime.*Timpprime.^-5)+B1prime); %define viscosity vector, viscosity in cP
nlog=log10(n);

%  plot(nlog,Timpprime)
```

```
% export data as spreadsheet in excel
% filename = 'Results1.xlsx';
% writematrix(n,filename,'Sheet','Visc vs Temp','Range','B3:B20') %shows viscosity values
% writematrix(Timpprimecelcius,filename,'Sheet','Visc vs Temp','Range','C3:C20')% shows Temperature values
% writematrix(Timpprime,filename,'Sheet','Visc vs Temp','Range','D3:D20')% shows Temperature values
% writematrix(nlog,filename,'Sheet','Visc vs Temp','Range','E3:E20')% shows viscosity values logarithmic
%Determine a range of temperatures
Tmin=20;
Tmax=420;
Tstep=10;
Trange(1,1)=Tmin;
for i=1:round(((Tmax-Tmin)/Tstep)+1)-1
    Trange(i+1,1)=Tmin+Tstep*i;
end
Trangek=Trange+273.15;

Tvisc=400+273.15;%Temp in K
%viscosity in relation of temperature
syms visc
Visc_log=solve(Tvisc == 3.6608*visc^2 - 54.187*visc + 543.12,visc);
Visc_result=(10.^Visc_log)/100; % visc in Poise
% Visc_result=10.^(.00013658*(54187-2.2361*(2928640.*Trange-1003356763).^.5))/100;
% Visc=10.^(.00013658*(2.2361*(2928640.*Trange-1003356763).^.5 + 54187))/100;
% visc=exp(-(10*(50.*Trange-23551))/4157);
```

APPENDIX B

Code in “m” language from MATLAB software for the calculation of pressure as a function of temperature

```
%% Pressure vs Temperature
%define constants
Tb=780; %K
% alfa=87060;
alfa=8.706;
beta=29.9;
gamma=.59;
M=300; %range 190-450
Twork=420+273.15; %K

%vapor pressure of petroleum derived product (Pa)
Pv1= (10.^(3.2041.*(1-.998.*(((Tb-41)./(Timp-41)).*((1393-Timp)./(1393-Tb))))))./1e-11;
%vapor pressure of petroleum derived product (atm)
Pvap1=(Pv1/101325)'; %atm
%vapor pressure of coal tar
Pvap2=(alfa*exp((-beta*M^gamma)./Timp))'; %atm

Ptot=Pvap1+Pvap2;

% export data as spreadsheet in excel
% filename = 'Results1.xlsx';
% writematrix(Pvap1,filename,'Sheet','Pressure vs Temp','Range','B3:B20') %shows Pvap of PDP values
% writematrix(Pvap2,filename,'Sheet','Pressure vs Temp','Range','C3:C20') %shows Pvap of coar tal values
% writematrix(Ptot,filename,'Sheet','Pressure vs Temp','Range','D3:D20') %shows total Pv
% writematrix(Timpprime,filename,'Sheet','Pressure vs Temp','Range','E3:E20')% shows Temperature values
%function
   Pv_PDP=(Trangek-372.97)/23.095;
   Pv_coaltar=(Trangek-213.62)/185.96;
Ptotal=Pv_PDP+Pv_coaltar; %Total pressure with temp range
```

APPENDIX C

Code in “m” language from MATLAB software for calculating coke formation as a function of temperature

```
%% Coke value vs Temp
%define constants
mass=33.33; %kg/h
k1=7.8589*10^8; %olefine
k2=2.099*10^12; %butadiene
k3=4.1865*10^8; %aromatics
E1=7.4164*10^4;
% E2=1.624*10^5;
E2=1.624*10^4.885;
E3=2.9977*10^4;
R=8.3143;
Farom=0.0329;
Fdiene=0.027;
Folefin=0.0695;
Molefin=0.511;
Mdiene=0.05;
Marom=0.40;
% kolef=6.71e-5;
% karom=4.66e-8;
kolef=5.01e-4;
karom=8.1e-9;

% Rolefin=k1*exp(-E1./(R.*Timpprimecelcius))*Molefin*mass*kolef;
% Rdiene=k2*exp(-E2./(R.*Timpprimecelcius))*Mdiene*mass;
% Rarom=k3*exp(-E3./(R.*Timpprimecelcius))*Marom*mass*karom;

% %kinetic of reaction
%equations for matching temperatures
Tolefin=-E1/(R*log(Folefin*mass/(k1*Molefin*mass*kolef)));
Tdiene=-E2/(R*log(Fdiene*mass/(k2*Mdiene*mass)));
Tarom=-E3/(R*log(Farom*mass/(k3*Marom*mass*karom)));
%fraction in mass
Rolefin=k1*exp(-E1./(R*Timpprime))*Molefin*mass*kolef; %chek kolef
Rdiene=k2*exp(-E2./(R*Timpprime))*Mdiene*mass; %check E2
Rarom=k3*exp(-E3./(R*Timpprime))*Marom*mass*karom;%check karom

% export data as spreadsheet in excel
% filename = 'Results1.xlsx';
```

```
% writematrix(Rolefin,filename,'Sheet','Coke value vs Temp','Range','B3:B20')
%shows Pvap of PDP values
% writematrix(Rdiene,filename,'Sheet','Coke value vs Temp','Range','C3:C20')
%shows Pvap of PDP values
% writematrix(Rarom,filename,'Sheet','Coke value vs Temp','Range','D3:D20')
% writematrix(Timpprimecelcius,filename,'Sheet','Coke value vs
Temp','Range','F3:F20')% shows Temperature values
% writematrix(Timpprime,filename,'Sheet','Coke value vs Temp','Range','E3:E20')%
shows Temperature values

%reaction with temp
Pdpmass=33.33;%kh/h
Cokingcole=0.8*Pdpmass;
coaltar=0.567*Pdpmass;
Treaction=280+273.15;% Temp in K
syms Rmass
R_olef=solve(Treaction == 370.33*exp(9.2158*Rmass),Rmass);
R_diene=solve(Treaction == 372.43*exp(21.31*Rmass),Rmass);
R_arom=solve(Treaction == 352.54*exp(21.083*Rmass),Rmass);
Coke_total=(R_olef+R_diene+R_arom)*Pdpmass+Cokingcole+coaltar;
```

APPENDIX D

Code in “m” language from MATLAB software for the calculation of the intrinsic characteristics of the final product such as the determination of the softening point, substances insoluble in toluene and substances insoluble in quinoline.

d1. Determination of the softening point

```
%% Softening point

Asp=4.57e14;%C aprox=[457036000000000] 4.57e14
% Sw1=zeros(18,1);
% Sw1(1,1)=10;
% for n=1:17
%    Sw1(n+1)=Sw1(1,1)+Sw1(n);
% end
% Asp=(0.358*Sw+4.82)*10e12;

%look at workspace for constant value
Sw=((Asp/10e12)-4.82)/.358;
```

d2. Determination of the substances insoluble in toluene (TI)

Using the Cornelissen & Waterman model

```
%% Insoluble toluene sust
B=0.2856;%calcualted from ref. data
% I1=zeros(18,1);
% I1(1,1)=5;
% for n=1:17
%     I1(n+1)=I1(1,1)+I1(n);
% end
Bprime=([-0.762 0.395 0.597 -2.117 -2.557 2.595 -2.339 0.872 -0.145 -1.871 ...
     0.52 -1.911 -0.2 0.185 -0.899 0.715 5.693 4.386])';
% B=.0191*I-.318;

 %look at workspace for constant value
I=(B +.318)/.0191;
```

Using the model of Shoko, et al.

```
%INPUT- Insoluble substances in toluene
CV=49.8696;
FC=79.63;
```

```
ash=0.17;
C=91.1;
N=1.4;
O=1.65;
moisture=1.66;
H=5.5;
S=.35;

TI= -40051.28+(0.56*CV)+(0.07*FC)-(2.4*moisture)+(10.63*ash)+(400.53*C)+(393.74*H)+(439.21*N)+(348.39*S)+(399.19*O);
```

The value of substances insoluble in toluene calculated using this model corresponds to 29.3912 %.

d3. Determination of the substances insoluble in quinoline (QI)

```
%INPUT- Insoluble substances in quinoline
SP=114.1899;
CV=49.8696;
FC=79.63;
ash=0.17;
vol=16.5;
C=91.1;
N=1.4;
O=1.65;
H=5.5;

QI=161.71-(0.12*SP)+(0.40*CV)-(3.10*FC)-(11.42*ash)-(3.04*vol)+(1.70*C)-(15.93*N)+(3.00*O);
```

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«_25_» _01_____ 2021.

MASTER´S THESIS

Modelling of Carbon Binder Obtaining in Flow Reactor

04.04.01 Chemistry
04.04.01.05 Petroleum Chemistry and Refining

Research supervisor ________ Ph.D., Associate Professor Vladimir Safin
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Graduate _____Herrera Stalin Fabricio Herrera Salinas
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Reviewer ________ Candidate of Chemical Sciences, Laboratory Scientist Anastasia Valerievna Obukhova
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Krasnoyarsk 2021