“Comparison of Petroleum Pitches prepared from Ethylene Tar Under Oxidative and Non Oxidative Conditions”

A Thesis

Submitted in the partial fulfillment of the requirement for the award of Degree

Of

Master of Technology
in
Refining and Petrochemical Engineering
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by

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Certificate

I hereby certify that thesis entitled **"Comparison of Petroleum Pitches Prepared from Ethylene Tar Under Oxidative and NonOxidative Conditions"** which is being submitted in the partial fulfillment of the requirements for the award of the degree of Master of Technology in Refining & Petrochemical Engineering of the University of Petroleum and Energy Studies Dehradun. University is a record of candidates own work carried out by him under the supervision and guidance of the undersigned.

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CERTIFICATE

This is to certify that the project work entitled "**Comparison of Petroleum Pitches Prepared from Ethylene under Oxidative and Nonoxidative Conditions**" submitted by Manoj Sharma (Roll. No. R080204004) in partial fulfillment of the requirements for the award of the degree of Master of Technology in Refining and Petrochemical Engineering at the College of Engineering, University of Petroleum and Energy Studies, Dehradun was carried by him under the guidance of Dr. Manoj Srivastav, Scientist "C", Lube and Wax Processing Lab, Indian Institute of Petroleum Dehradun. This work has not been submitted else where for a degree or diploma.

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EXECUTIVE SUMMARY

The objective of the proposed study is to prepare Pitches under oxidative (Air, oxygen and catalyst (acetic acid +nitric acid)) and non-oxidative conditions and to study the differences in properties of the pitches such as Softening point, Coking value, Quinoline insolubles, Toluene insolubles and NMR analysis, so prepared and their suitability for specific end-use applications.

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Chapter -1

INTRODUCTION

Pitches are complex mixtures of polynuclear aromatic hydrocarbons which are thermoplastic in nature and their alkyl or hydroxyl derivatives and the corresponding heterocyclic analogous containing oxygen, nitrogen or sulphur. The molecular weight of these compounds ranging from 200 to 3000 with an average of 400-600 Daltons.

Pitch is an essential constitution for making all types of carbon materials. In conventional binder fillers method for making carbon/ graphite aircrafts, pitch is used as binder and impregnating agent. Thus pitch is basic raw material for various carbon materials like activated carbon, CMS, fullerenes, mesocarbon, mesobeads, carbon fibres, and carbon-carbon composites. In terms of consumption, graphite electrode industry is the main consumer of pitches. Two types of pitches, binder and impregnating are used in the fabrication of graphite electrodes. Binder pitches are used to hold carbon aggregate together during moulding and baking. Impregnating pitch is a very specialized product and is used to reduce the porosity and increase the density of baked carbon body prior to graphitization.

Petroleum Pitches are used in the fabrication of carbon electrodes and there are two types of pitch used:

Binder pitch: holds the carbon aggregate together during the moulding and baking of the carbon body. They are highly polymerized aromatic hydrocarbons, which are solid at room temperature.

Impregnating pitch reduced the porosity and increased the density of the baked carbon body prior to graphitization. They must be fluid enough at the impregnating temperature to enter the pore structure at the carbon body.

The aluminum industry is the largest consumer of carbon electrodes and heavily influences demand for electrode pitches. Compared to binder pitch, impregnating pitch has lower softening points, TI and QI. Suspended particles and other QI in the pitch would reduce the infiltration rate by forming a boundary layer on the carbon body. Originally coal tar pitches were the only source of electrode pitch, but as the demand grew, coal tar supply became inadequate in the quantity and quality. Coal tar pitch has lower sulfur and higher aromaticity than petroleum pitches.

Since pitches feed stocks are complex mixture of hydrocarbons, it is difficult to predict the behavior of feed stocks during pitches this has led to the concept of determination of parameters to represent them. Average structure parameters are obtained from ^{13}C and ^{1}H NMR spectroscopy together with elemental analysis and number average molecular weights.

It can be seen from the data in tables that petroleum pitches are highly aromatics with low heteroatom contents. However petroleum pitches have higher sulfur content but lower nitrogen contents than coal tar pitch.

Preparation of pitches is greatly affected by thermal soaking in presence of different type Nonoxidative and oxidative gases. Preparation of pitch under oxidative or non-oxidative conditions has great influence on pitch properties as well as final product quality. Pitches are prepared from petroleum and coal based sources. Although preparation of pitch under non-oxidative conditions is desirable for making graphite electrodes, but in certain cases preparation of pitch in oxidative condition is more useful as it greatly enhances the desired properties of pitch needed for production of certain carbon materials such as activated carbon fibers and activated carbon spheres

Chapter-2
LITERATURE REVIEW

Pitches are excellent precursors for a no of advanced carbon materials such as Electrodes, carbon fibers, carbon molecular sieves, mesocarbon, carbon beads, activated carbon spheres, needle cokes etc.

Pitch is generally prepared by thermal treatment of aromatic rich residues from various petroleum refining and petrochemical processes. The inherent complexity of petroleum residues increases the pitch complexity many more times. The properties of pitch are largely dependent on feed properties. Thermal treatment temperature, residence time, pressure and additives used. The proper selection of these variables leads to formation of desired quality product.

2-1. **Pitch feed stocks**

The selection of the feedstocks is the main concerned for the preparation of good quality pitch.

Principle sources of making carbon materials are coal, and petroleum. Conventional source for carbon materials is coal tar but in recent years, coal tar supply became inadequate due to closure of several coke ovens in many parts of the world resulting from environmental protection agencies regulations. Many petroleum derived aromatics rich feed stocks seem to be a good alternate to coal tar. These feedstocks are by-products of thermal and catalytic conversion processes practiced in refineries and petrochemical plants.

Petrochemical producers generally consider these by-product streams, as a low value product mainly further processing of these into more valuable products is very difficult and expensive. Thus producers of these streams refer to these materials as "fuel oil". Currently use of fuel oil in furnaces has been inhibited because the combustion of this oil particularly of those, which have high sulphur concentration, produces sulfurous acid gas result in atmosphere pollution. As these petroleum streams are available with their producers in large volume at a low cost, another option for their use is to make industrial carbons from them, which is more appropriate because they have high carbon content.

Heavy aromatic oils (HAO) have a carbon contents and are used as feedstocks for the manufacture of electrode pitches. These feed stocks are by-products of petroleum refining, petrochemicals manufacture and coal coke production. Most of the feedstocks are petroleum derived but coal derived HAO must be considered because it is an important supply source in certain countries.

The so-called heavy aromatics oils contain polynuclear aromatics such as naphthalene, anthracene, chrysene and Pyrene, which are synthesized during the processing of petroleum and coal.

The major sources of heavy aromatic oils are:

Decant oil from catalytic cracking of atmospheric and vacuum gas oil to produce gasoline and middle distillates.

Ethylene Tar from steam cracking of naphtha and gas oils to produce ethylene.
Coal tar oils produce during coal coking or gasification.

Thermal tar from thermal cracking of atmospheric and vacuum gas oil to produce gas oil and middle distillates.

In the first three instances, the HAO is an unavoidable by product.

The major properties requirement of pitch feedstocks is as follows;

- Aromaticity is generally measured by the Bureau of mines correlation index (BMCI). It is an indication of the carbon to hydrogen ratio.
- Sulfur content is of concern for product quality and environmental reasons. Viscosity must be low enough that the HAO can be easily handled in cold weather.
- Gravity is a rough indication of aromaticity and boiling range, carbon feedstocks are heavier than water.
- Contaminants such as ash, coke particles, Na and K must be low to insure product quality.
- Solvent insolubles are measured in various ways.
- Binder pitch producer wants high contents of benzene insoluble compounds.
- Flash point is an important safety consideration.

HAO Sources

Fluid catalytic cracking is the major process that refiners use to convert atmospheric and vacuum gas oil into higher priced gasoline and heating oil. The heaviest product is decant oil which has an initial boiling point of 345°C and represents 2-7 volume % of the total products. Some people use the terms clarified oil or FCC fractionator's bottoms. Decant oil is very important precursor for the petroleum pitch.

Steam Cracking

Steam cracking of petroleum products ranging from ethane to gas oil is used to produce ethylene, with the heavier feedstocks producing more co-products such as propylene, butadiene and benzene. Naphtha and gas oil cracking produce a 205+°C, highly aromatic, byproducts oil, which is called ethylene tar or Pyrolysis fuel oil. In a naphtha cracker, the quantity is so small that generally the oil is produced as a single stream. The larger quantity produced by gas oil cracking is generally fractionated into a naphthalene concentrate (Pyrolysis gas oil) cut boiling roughly form 205 to 285°C and a 285+C Pyrolysis tar (aromatic tar).

Pyrolysis Tar needs special attention because in most instances it is highly unstable and incompatible with other fuels. Most Pyrolysis tar is used as plant fuel for steam generation or sold as feedstocks for carbon.

Typical properties of ethylene tars from naphtha and gas oil cracking are shown in table:

	Decant Oil	Ethylene Tar #1	Ethylene Tar #2	Cresote Oil
Sulfur, wt%	0.7 to 4	0.05 to 0.1	0.2 to 1.5	0.1 to 0.6
Ash, wt%	0.02 to 1	<0.01	<0.01	<0.01
Pentane insolubles, wt%	1 to 8	10 to 15	20 to 35	1 to 3
BMCI	110 to 135	125 to 140	125 to 140	140 to 160
Gravity				
Specific	Up to 1.13	1.04 to 1.08	1.07 to 1.12	1.07 to 1.16
^{O}API	+10 to -6	+4 to -1	+1 to -5	+1 to -9
Distillation (760mm) °C				
IBP	315 to 345	195 to 215	235 to 290	205 to 260
50%	370 to 430	260 to 290	290 to 345	290 to 370

Notes: ethylene tar #1 is representative of the 205+°CPyrolysis oil produced in a naphtha cracker. Ethylene tar #2 is representative of the 285+°C Pyrolysis tar produced by a cracker using hydro treated gas oil feed.

Ethylene tar have much lower sulfur levels than decant oils, because naphtha naturally has low sulfur, while most gas oil used as ethylene feedstocks is generally desulfurized.

2-2. Characterization of Feedstock

The feedstock (ethylene tar) used in the present study for making pitches has been characterized by Physico-chemical properties, which are given in table:

Property	**Ethylene tar (pyrolysis tar)**
Density (g/ml)	1.0443
Kin. Viscosity,(cSt) at 100oC	1.73
Adv. Mol. Wt.(Dalton)	206.0
Pour point,(oC)	-24.0
Flash point,(oC)	69.5
Coking value,wt%	10.67
BMCI	126

1HNMR	
Har	61.12
Hα	27.77
Hβ	9.09
Hγ	1.52
Har(mono)	9.09
Har(di)	51.01
Har(poly)	1.52
Ar-CH2-Ar	4.04
αPh	24.24
βN	4.04
βCH2	5.05
γCH3	1.52

The examination of physico-chemical data of feedstocks shows that aromaticity for ethylene tar is high. It seems to be a good feedstock for pitch production.

Basic Pitch Properties:

They are some basic properties for the determination of the quality of petroleum pitch. These properties are required for the selection of pitches for manufacturing electrode and carbon material. The brief discussions of properties are given as follows:

Softening Point:

The softening point of pitch is measured using a Mettler Toledo FP 90 following the ASTM 3104 standard procedure. A small cup (with a pierced bottom) was filled with approximately 0.5gm of pitch. The cup was placed in the Mettler furnace and preheated to 20°C below the expected SP. Then, the oven temperature was increased at a rate of 2°C until a drop of pitch passed through the hole, this point representing the softening temperature of the pitch.

And this also indicates the flow properties of the pitch.

Pitch Insolubles

This property is used for the determination of the insolubilities of pitch. The insolubility of pitch is determined in Quinoline (QI) and Toluene (TI)

- **Quinoline Insolubles (QI)**

ASTM D-2318 is the standard method for determination of QI. The principle of the determination of quinoline insoluble in pitch involves digesting the sample in hot quinoline to decrease its velocity and filtering the solution. The insoluble material is washed, dried and weighed and its determination in wt%.

- **Toluene Insolubles (TI)**

ASTM D-4312 is the standard method for determination of Toluene Insolubles.
This test method covers the determination of toluene insoluble matter TI in pitch.
This test method is useful for evaluating and characterization of pitch is one element in establishing the uniformity of shipment of sources of supply.

- **Coking value**

Coking value is determined by using micro carbon residue Tester Model ACR- M3 by TANAAK SCIENTIFIC LIMITED.

The pitch is carbonized under nitrogen flow by increasing the furnace temperature to 900°C at a rate of 5°C per min., this temp being maintained for 30 min. pitch carbon yield calculated from the weight of carbonaceous residue.

- **Beta Resin**

Beta resin is the mathematical difference between toluene insoluble and quinoline insolubles and represents a large polynuclear molecular weight portion in pitch.

$$\text{B- Resin} = \text{TI-QI}$$

- **Elemental Analysis**

The carbon, hydrogen, sulfur, nitrogen contents determined with a LECO-CHNS –932 microanalyser. The oxygen content measured using a LECO-VTF-900 furnace coupled to the same microanalyser

2-3. Chemistry of petroleum pitches, prepared under different conditions

Generally pitches are prepared by thermal soaking of aromatic rich feedstocks. Thermal soaking in presence of different gases such as nitrogen, air, oxygen and presence of liquid catalyst changes the find pitches properties. The possible mechanism of pitches formation in presence of liquid oxidizing agent may be depicted as below

2-3-1. Thermal soaking

Chemical reactions involved

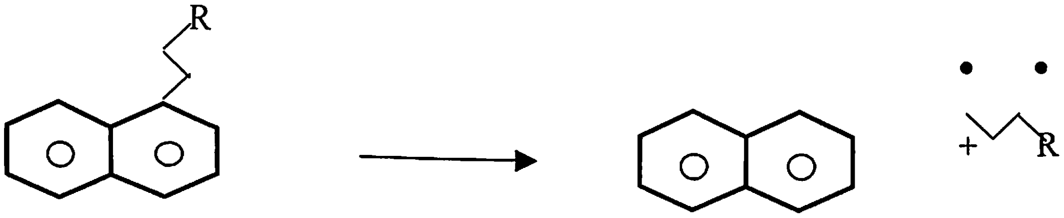
The thermal soaking reactions takes place at high temperature (350-450°C) for the conversion of ethylene tar into petroleum pitch in the presence of nitrogen gas at a flow rate of 150ml/min, nitrogen gas create inert environment for the reaction.

In reaction systems the increase in soaking time will give rise to the formation of mesogen. The main chemical changes associated with the heat treatment of pitches involve thermally induced polymerization, which can be monitored to an extent by the change in insoluble content of the pitch. The extent of polymerization during the conversion of tar to pitch can be obtained through molecular weight distribution, determined by gel permeation chromatography The chemistry of formation of carbonaceous pitch can be understood from the thermal reactions of individual components of pitch. The major changes that take place involve, molecular rearrangement, cleavage of side chains and polymerization. For aromatic hydrocarbons contained alkyl substituents, the cleavage of side chains provides a route for subsequent polymerization. Polymerization of aromatic hydrocarbons through dehydrogenation gives rise to two types of polymers. The first involves the loss of two hydrogen atoms between two reacting aromatic molecules through a coupling reaction. The resulting products are aryl-aryl polymers, which can be non-planar due to free rotations about the connecting aryl–aryl bond. The second type of polymer involves an aromatic condensation through the formation of another aryl-aryl hand between reacting units. The condensation process results in the formation of more highly stabilized free radicals thus slowing the overall polymerization process.

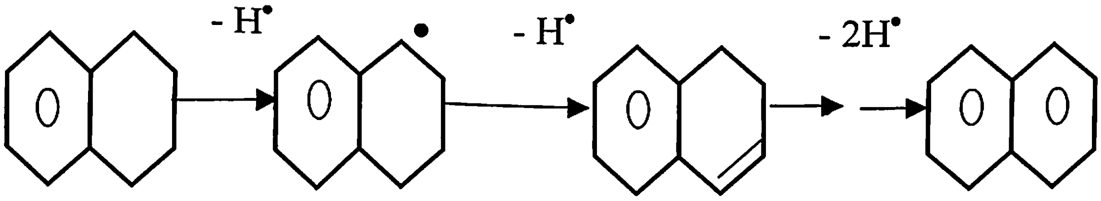
MECHAINSM OF PITCH FORMATION

The conversion of aromatic rich feedstocks into pitch is very complicated process. This conversion proceeds through free radical mechanism. During thermal soaking, aromatic components of the feedstock undergo following reactions:

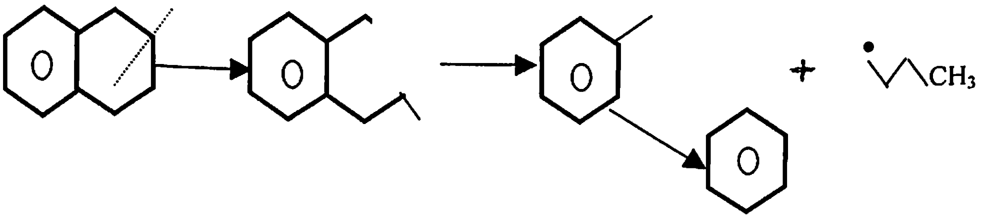
Elimination of Side Chains



Dehydrogenation of Naphthenes into Aromatics

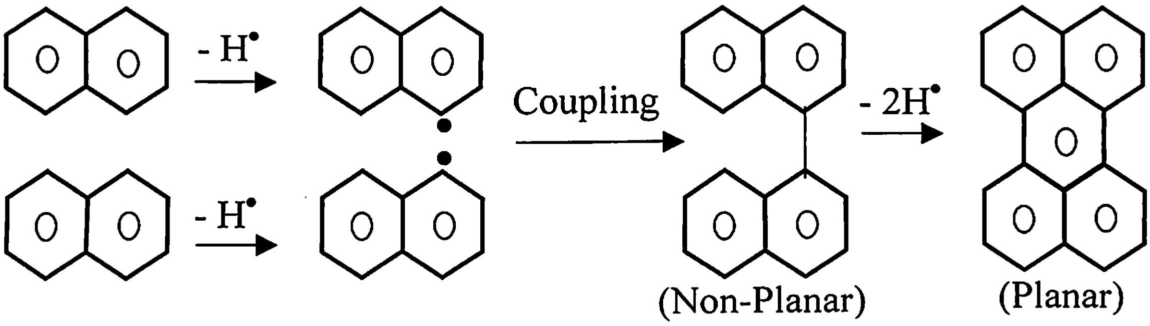


Ring opening reactions



CH_3

Polymerization and Condensation



These reactions convert smaller aromatics (2, 3, 4, membered) into polynuclear aromatic hydrocarbons PAHs (MW 500-600) that is designated as pitch. This pitch is 'isotropic' in nature.

2-3-2. Oxidation

Oxidation takes place in presence of air, oxygen and catalyst

2-3-2; (a). Reaction with Air

Raising the softening point of petroleum pitch has been achieved by air blowing, because the air blowing reaction more effectively increases coke yield than heat treatment, distillation or other methods.

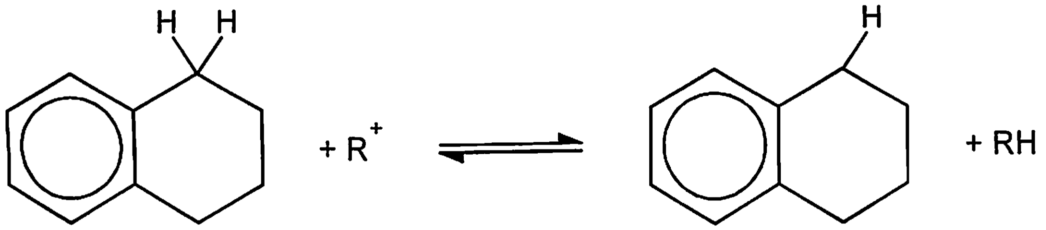
The air blowing reaction shows every indication of raising the softening point and increases the insolubles for solvent and the carbon hydrogen ratio. Also the air blowing reaction suppresses the growth of mesophase phase in the isotropic matrix.

Structural changes in the pitch during the air blowing reactions based on NMR, IR & other measurements, where carbon in the Alpha position of alkyl aromatic compounds in source materials pitch is attacked by oxygen. This results in cross linking such as ether bonding as well as condensation reactions mainly involving dehydrogenation by oxygen. Polymerization is accelerated by the biphenyl type condensation reactions .It is believed that air-blowing reactions proceeds via radical mechanism the auto oxidation of alkyl benzene and other compounds are typical examples.

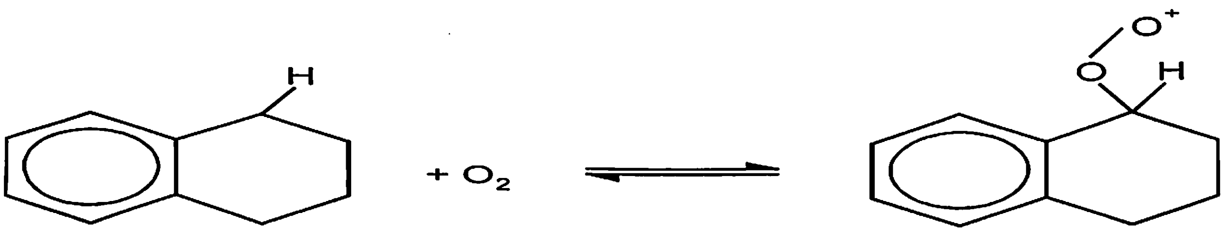
The rate of oxidation at high temperature is determined by the diffusion control of oxygen. Since the aromatics hydrocarbons are viscous liquids during the reaction, it is suggested the reaction system is under the condition of oxygen shortage. The cross-linked methylene group bonding, biphenyl type bonding, and ether bonding are formed thought the termination reaction of the species with radicals. Carbonyl bonding is thought to be generated by subsequent oxidation of cross-linked methylene groups. When subjected to oxidation in air at 350-450° C, alkyl substituted aromatic compounds polymerize with methylene, biphenyl type and ether bonding, leading the methylene to partially change into carbonyl during air blowing reactions.

A proposed mechanism for the initial stage of oxidation, resulting in weight gain by uptake of oxygen as ketone functional groups and the loss of methylene hydrogen is illustrated in figure. 1

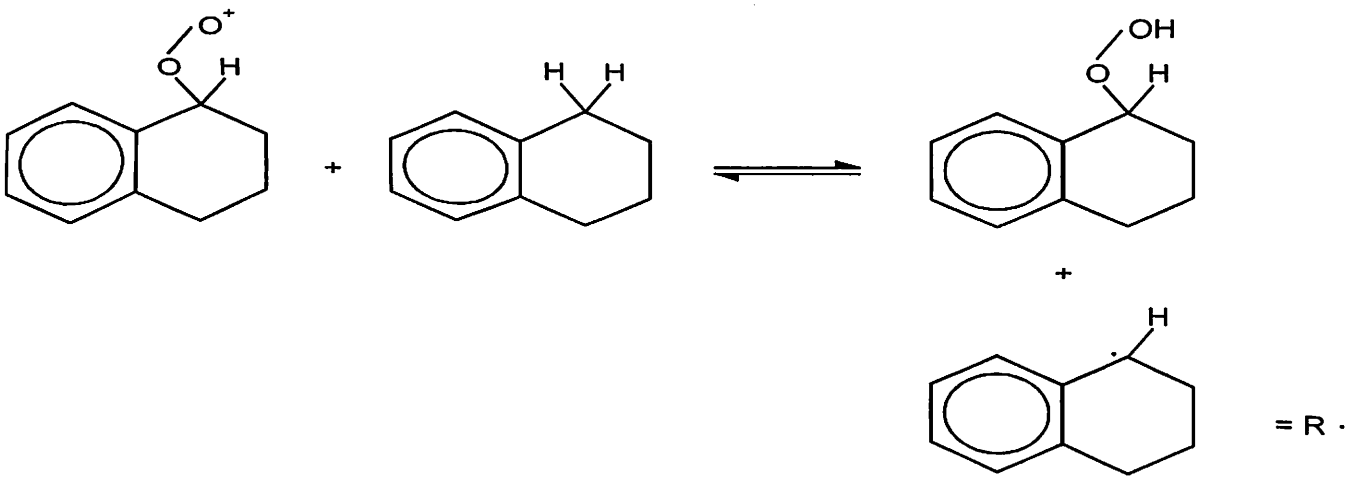
Radical initiation



Attack by oxygen



Hydrogen abstraction and propagation



Concerted peroxide decomposition with production of water

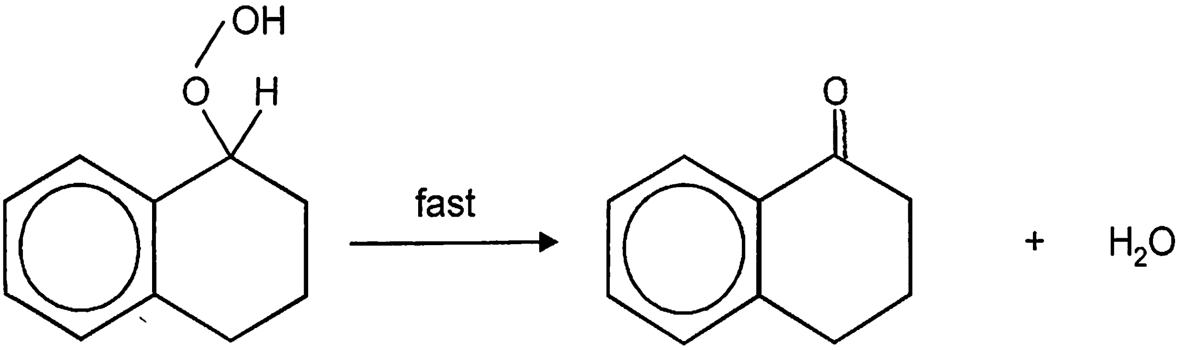


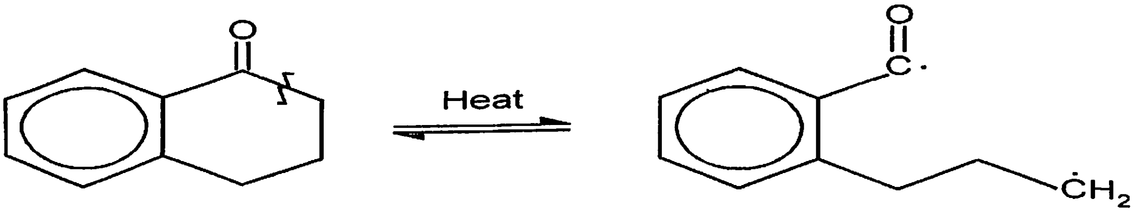
Figure 1. Mechanism for initial weight gain during oxidation through ketone formation via a hydroperoxide intermediate.

The mechanism also satisfied the requirement for the production of H2O, as a result of decomposition of the peroxide intermediate. It efficiently represents the primary oxidisable chemical structures present in our synthetic pitch, which contains both aromatic and aliphatic carbons, along with aromatic and methylene hydrogen's. The mechanism sketched in figure 1 shows the resultant addition of one oxygen atom with the loss of two-methylene hydrogen and the production of one molecule of water to for the ketone and produce a net weight gain of 10.6%. It is possible for the saturated naphthanic ring of the tetra hydro naphthalene molecule to add more than one oxygen atom, with further loss of methylene hydrogen emission of water and ketone production. We may add that the theoretical percent weight gain for this process is close to the experimental maximum percent weight gain was 10.7% achieved.

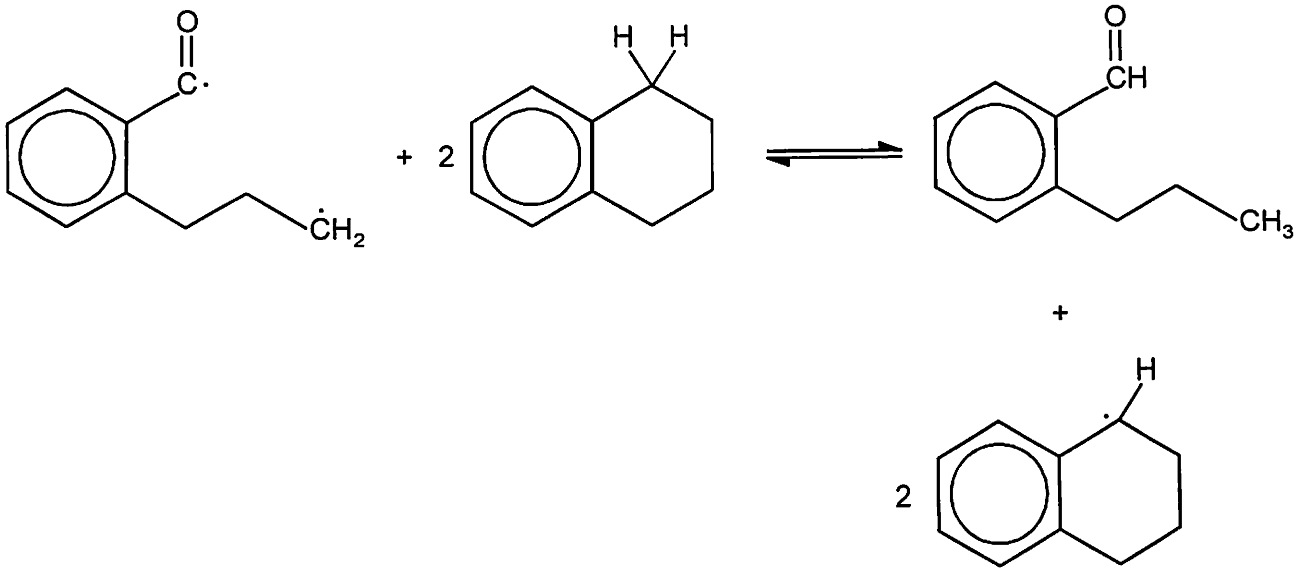
We must also be able to describe the formation of oxygenated cross links between pitch molecules, so essential for the production of a high coke yield with reduced fusion and associated with a reduced production of oligomers during carbonization. Simple and direct routes for the formation of aldehydes and carboxylic acids from ketone precursors are illustrated in figure 2.a &2.b

a

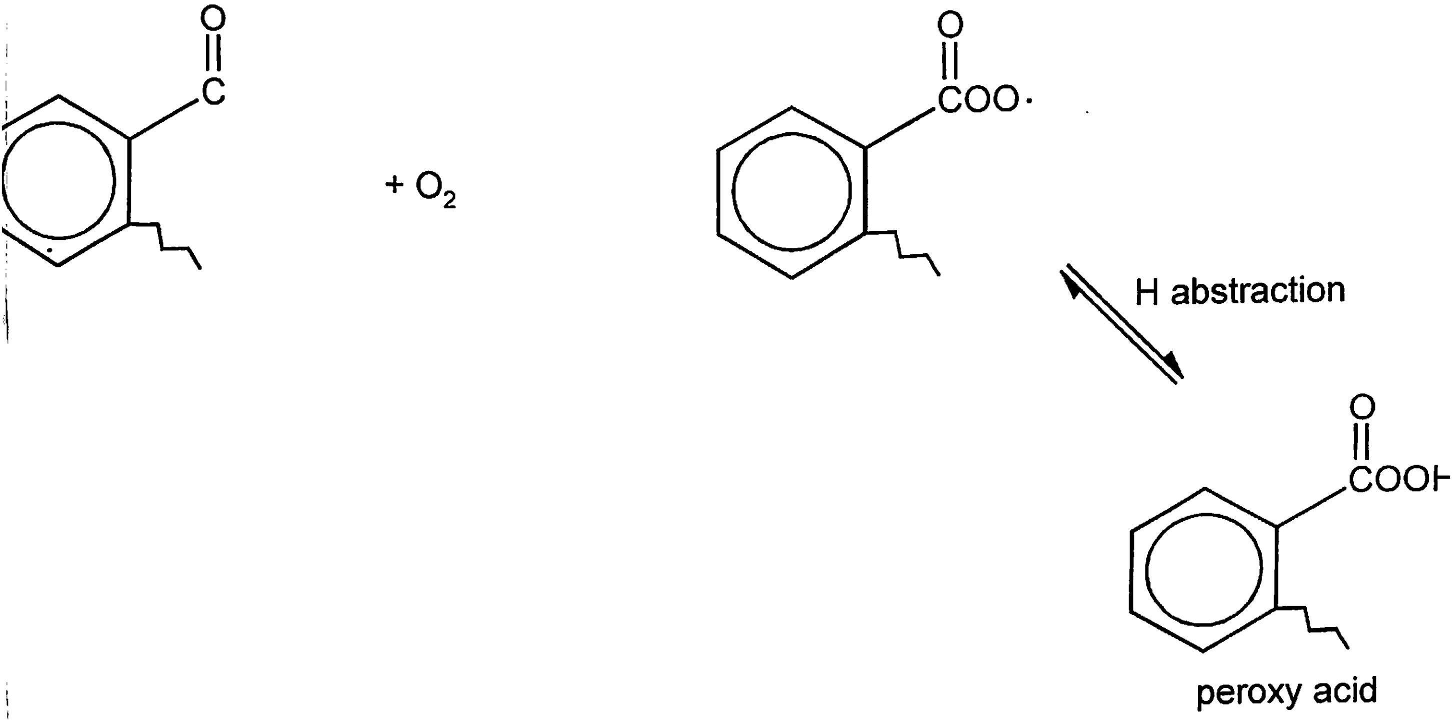
Thermal bond scission



Hydrogen abstraction to form aldehydes



b .Attack of oxygen to form peroxy acid



b. Decomposition of peroxy acid, Formation of Carboxylic acid

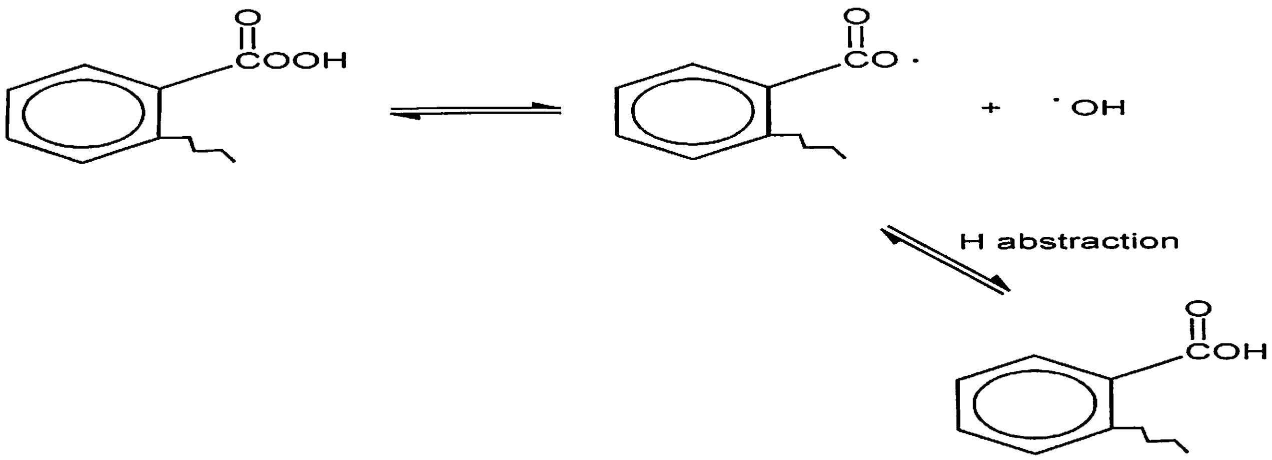


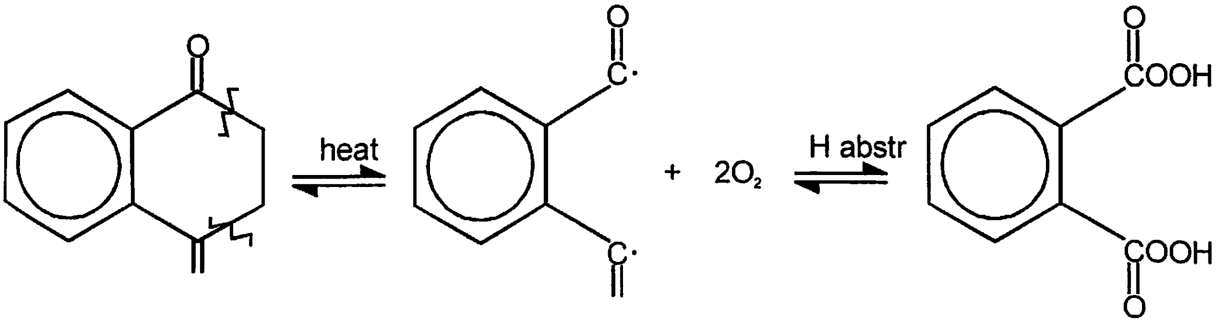
Fig.2; Alpha-keto bond scission followed by (a) hydrogen abstraction enroute to aldehyde functionality (b) by peroxy acid formation enroute to carboxylic acid functionally

Both mechanisms involve alpha keto bond scissions followed by the abstraction of hydrogen by a radical intermediate. Peroxy acid is mostly formed from the attack of oxygen on the radical formed by the alpha keto bonds scission. This second radical can abstract hydrogen to form the peroxy acid intermediate. Decomposition of the peroxy intermediate followed by hydrogen extraction yields the carboxylic acid functionality as illustrated in figure 2.b

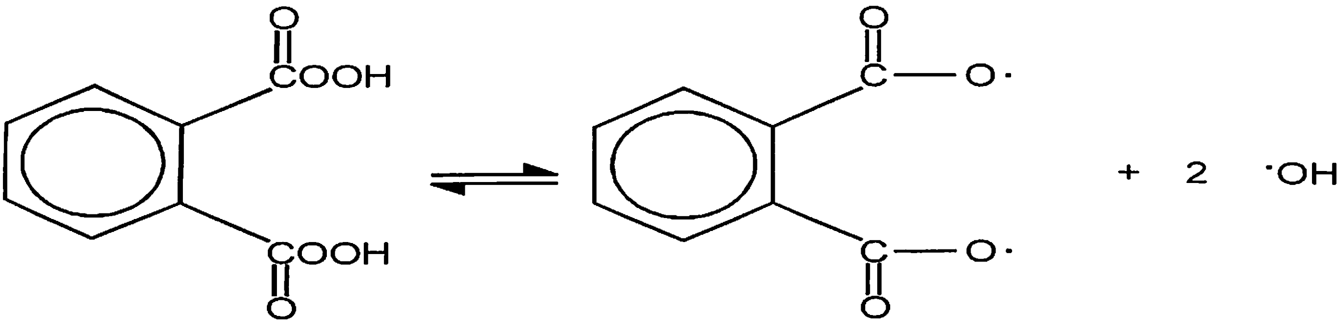
The diacyl peroxide may be formed intra molecularly or inter molecularly as shown in figure 3a & 4a.

a.

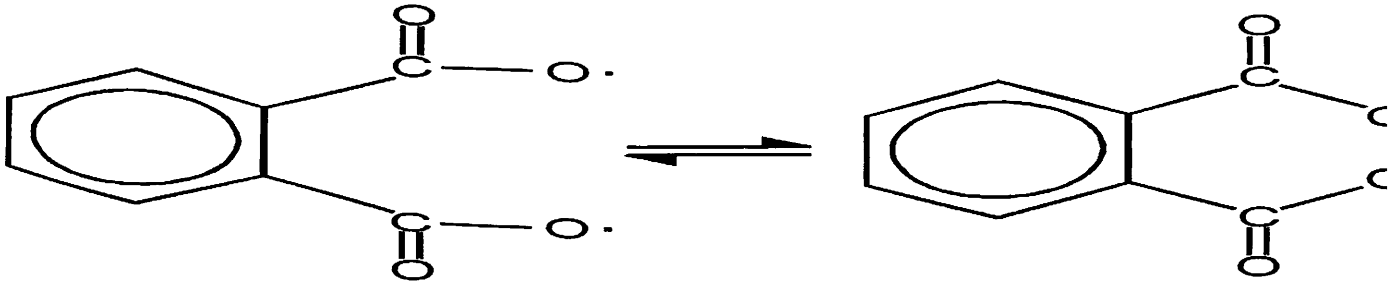
Formation of peroxy acid



Peroxy acid decomposition

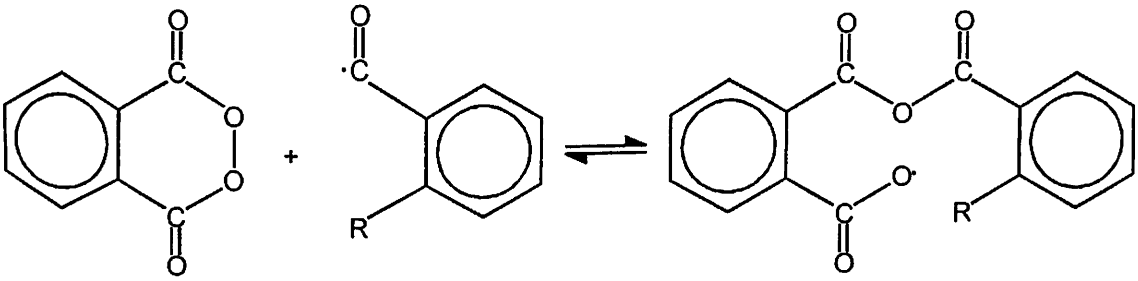


Formation of Intramolecular diacyl peroxide



b.

Direct displacement by second radical



Carbon dioxide formation

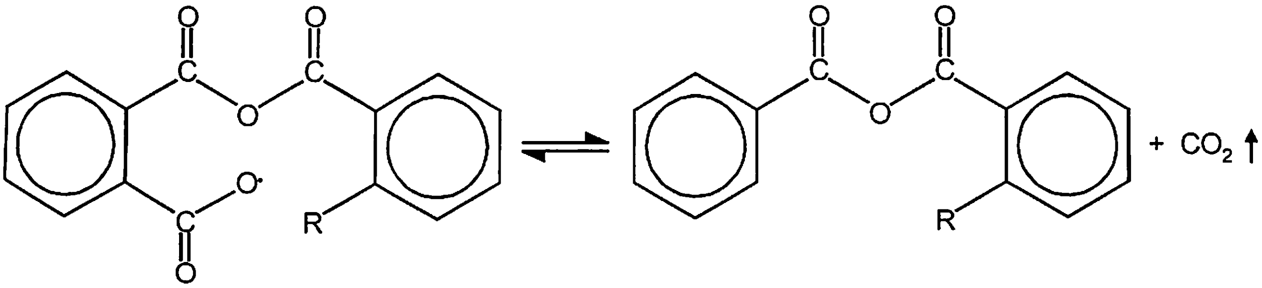


Fig.3(a) Formation of Intramolecular diacyl peroxide; (b) direct displacement of Intramolecular diacyl peroxide.

In either case, the diacyl peroxide then undergoes direct displacement by a second aldehydic radical intermediate to yield an anhydrous cross link. Subsequent mechanism pathways for the formation of carbon dioxide are studied in figure 3b.

The operation of this type of decomposition reactions would come therefore, act to transfer the overall ordering of the pitch precursor to the carbon product.

Raising the softening point of petroleum pitch has been achieved by air blowing, because the air blowing reaction more effectively increases coke yield than heat treatment, distillation or other methods.

The air blowing reaction shows every indication of raising the softening point and increases the insolubles for solvent and the carbon hydrogen ratio. Also the air blowing reaction suppresses the growth of anisotropic phase in the isotropic matrix

2-3-2.(b) Reaction with oxygen

Chemistry

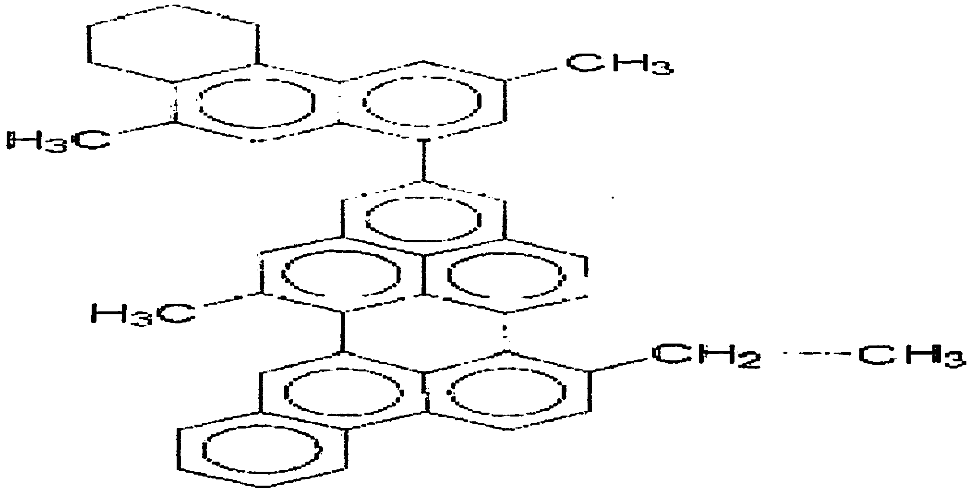
The oxidative stabilization of a synthetic, naphthalene –derived pitch was characterized in a dynamic oxygen atmosphere using material subjected to different time profiles of oxidation. It is concluded that oxidation involves processes that result in both weight gain and weight loss, with weight gain occurring rapidly during the early stages of oxidation accompanied by an uptake of oxygen and a loss of aliphatic content from the pitch. The weight loss regime was associated with the longer time periods or higher temperature of oxidation, and was found to result increase in the relative oxygen content in the pitch.

Diffusion of oxygen into pitch;

The physical diffusion of molecular oxygen into the pitch is in the cross-linking and polymerization processes which lead to the infusibilization (thermosetting) of pitch by air or oxygen. These processes are of obvious importance in the transformation of pitch in bulk, particle or fiber form to carbon and graphite.

The process of physical diffusion of molecular oxygen into pitch can be monitored by measuring the EPR (electron paramagnetic resonance) radiation behavior of the naturally occurring free radicals in pitch.

The chemistry of the reactions with oxygen on the basis of a model molecule shown in fig.



It has been proposed as a structural model of a typical molecule of petroleum pitch .The investigations by FTIR and XPS have clearly shown the following oxygen containing functional groups such as hydroxyl carbonyl & carboxyl. In the formation of these functional groups only water is formed as a volatile reaction product.

Carboxyl and hydroxyl groups may under the consecutive condensation reactions with the formation of carboxylic anhydrates, esters and water as the volatile product. These reactions may occur intra or intermolecularly.

Most important are cross-linking reactions by formation of C-C bonds. If oxygen-containing functional groups are involved in these reactions, CO_2 & CO is evolved as volatile products. Although carboxylic groups may be thermally very unstable it is suggested that such reactions are primarily occurring at an early stage of pyrolysis.
Including the later reaction possibility from the following reactions should be important for the increased coke yields of the pitch.

(1) Formation of oxygen containing functional groups, where by water is formed as the volatile product. The hydrogen evolution should be negligible in respect to the mass change, the mass gain may be attributed to the uptake of oxygen.

(2) Intra &inter molecular cross linking reactions between oxygen containing functional groups, the formation of water as the only volatile product should not influence the mass change of the pitch

(3) Inter molecular cross-linking reactions and formation of C-C bonds, induced by dissociation reactions of oxygen containing functional groups. It is highly probable that these cross-linking reactions occur to a much lower extent during the oxygen treatment then during the early stages of pyrolysis. In some reactions CO_2 &CO are additionally formed as volatile products. This clearly led to a mass loss that cannot be neglected.

All the above-mentioned points are discussed in the figure 6.

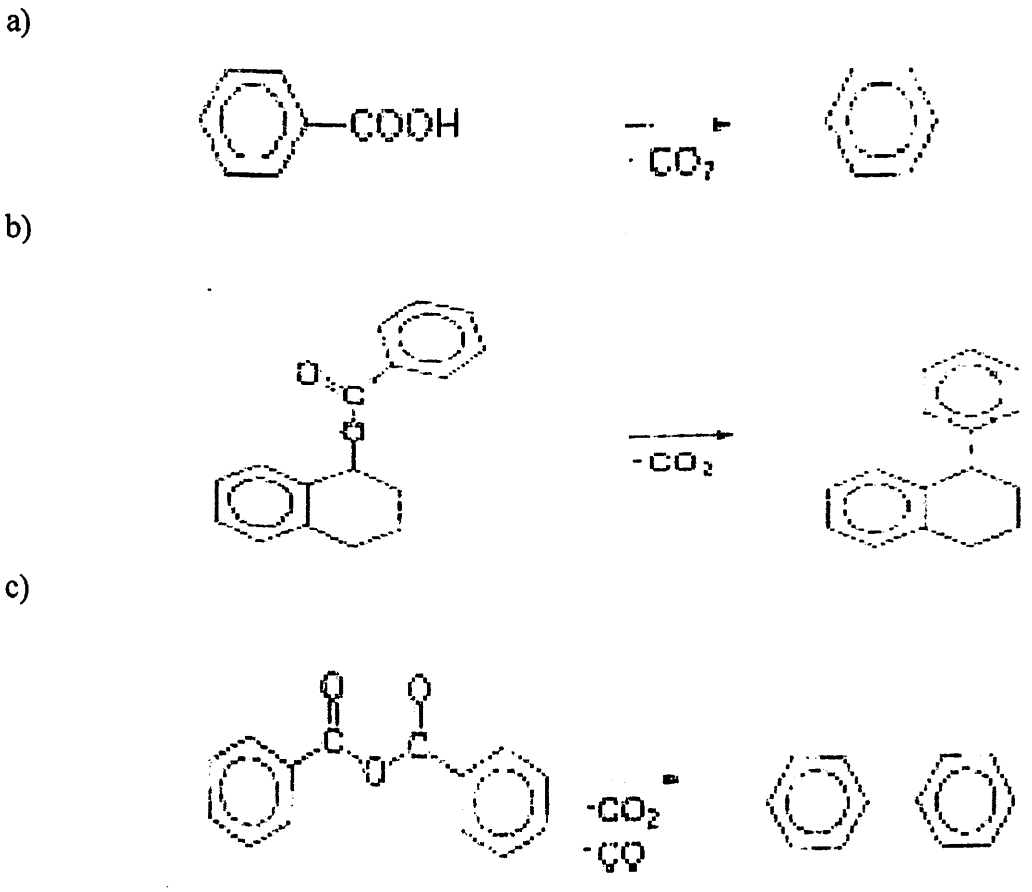


Fig.6. Dissociation reactions of pitch molecules cross-linked by oxygen

It is assumed that the reactions described above contribute to the stability of pitch mainly in the temperature range in which volatile pitch constituents usually evaporate.

2-3-2.(c). Reaction with catalyst (Acetic Acid+ Nitric Acid)

Chemistry

Preparation of carbon fibres from pitches involves spinning, stabilization and carbonization. Carbonization consists of the pyrolysis of stabilized fibres to increase their carbon content. Usually, spinning of the parent pitch and stabilization of the pitch fibres are the key steps in the thoroughly of carbon fiber preparation.

A suitable precursor must fulfill some initial requirements

1. The softening point must be higher, because pitch lower softening point cannot be easily stabilized in air for a reasonable time.
2. It is desirable to start from a completely isotropic material because it would permit an easier spinning.
3. Another important point is the absence of infusible matter that decreases the spin ability of the pitch and reduces the mechanical properties of the carbon fibres.

And finally appropriate rheological properties, involving appropriate viscosity that permit the pitch to soften and flow properly. Then, pitches for preparation of carbon fibres must have both a high spin ability (related to its rheological properties) and a high softening point, unfortunately both properties change in opposite trends that is the spinnability of the pitch decreases with increasing SP and a compromise between both parameters is necessary. From the above, we can conclude that most of the commercially available pitches are not useful for carbon fiber preparation due to their low softening point. Then their use in this application requires applying an appropriate treatment to increase the softening point of the raw material or to develop an alternative stabilization method suitable for low softening point pitch fibres.

In this work we have studied the stabilization of pitch fibres with low softening point by a treatment with a Nitric and Acetic acid aqueous solution. The influence of the HNO_3 concentration on the stabilization of the pitch fibres and the properties of the carbon fibres obtained have been analyzed.

Chapter 3.
EXPERIMENTAL

3-1. Experiment 1

Synthesis of petroleum pitch from ethylene tar by simple distillation method in the presence of nitrogen gas.

Pitches were prepared by thermal treatment of feedstocks in a glass reactor equipped with a condenser to collect the distillate.

A thermal treatment of ethylene tar under atmospheric pressure in the presence of nitrogen gas by distillation produced a pitch of high softening point with a high coking capacity. Arranged the apparatus as shown in fig which has given below.

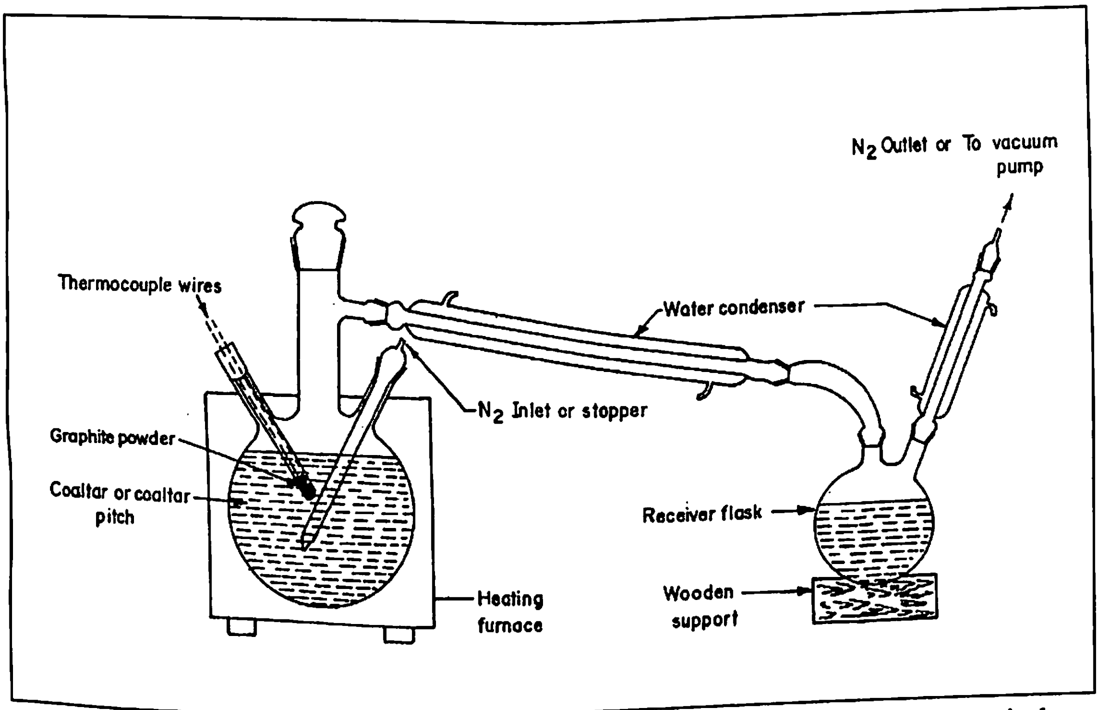


Figure- A sketch diagram for the development of performing pitch

Procedure

Weighed the reaction vessel and receiver; charged the feedstock (ethylene tar) weighing 80g into round bottom flask. Now start passing currant through the heating element such that the temperature of feed stocks raised to 200°C now allow nitrogen at a flow rate of 200ml/min into the reaction vessel through gas stripper, increase the temperature and set in the range of 350-450°C. This reaction took place at atmospheric pressure. The drop of distillates enters the receiver at temp of 250°C. It has been observed that the rate of receiving the distillates was relatively high for the first four hours and later the distillates rate reduced.

The reaction is progressed for 5:00 hrs the empty the reaction vessel at 200°C into the glass bowl. It had been observed that some gasses are escaping with nitrogen through the receiver by performing material balance of the feed and the distillates +residue.

The residue from the flask was sent for the further analysis such as softening point determination, QI, TI, Coking value, beta resins.

Material Balance:

Weight of empty reaction vessel 500ml (a) = 138.3g
Weight of gas stripper (b) = 24.6g
Weight of thermometer pocket (c) = 18.3g
Total weight of reaction vessel
RV= a+b+c = 181.2g
Amount of sample charged, SC = 80g
Weight of sample charged and reaction vessel, A = SC+RV
= 261.2g
Weight of receiver, R = 171.8g
Weight of receiver and distillates (after 5hrs.),
B = R+D = 198.3g
Amount of residue and reaction vessel
C = P+RV =234.4g
Amount of pitch, P =C-RV
234.4-181.2 = 53.2g
Amount of distillates, D = B-R
198.3-171.8 = 26.5g

Weight of gas + losses, L = SC- (P+D)
80-(53.2+26.5)
= 0.3g

Wt% of residue, P = 66.5 wt%
Wt% of distillates, D = 33.1 wt%
Wt% of gas + losses, L = 0.37wt%

Input = Output
80g Residue + Distillates + Gas losses
(Sample) 53.2g +26.5g + 0.3g
= 80g

3-2. Experiment 2

Synthesis of petroleum pitch from ethylene tar by simple distillation method in the presence of air.

The reaction was progressed for 5:00hrs the empty the reaction vessel at 200°C into the glass bowl. It has been observed that some gasses are escaping with air through the receiver by performing material balance of the feed and the distillates +residue.

Material Balance:

Weight of empty reaction vessel 500ml (a) = 38.1g
Weight of gas stripper (b) = 24.2g
Weight of thermometer pocket (c) =18.0g
Total weight of reaction vessel
RV= a+b+c = 180.3g
Amount of sample charged, SC = 80g
Weight of sample charged and reaction vessel, A = SC+RV
= 260.3g
Weight of receiver, R =152.1g
Weight of receiver and distillates (after 5:00hrs.),
B = R+D = 188.2g
Amount of residue and reaction vessel
C = P+RV =225.8g
Amount of pitch, P = C-RV
225.8-180.3 = 45.5g
Amount of distillates, D = B-R
188.2-152.1 = 36.1g

Weight of gas + losses, L = SC- (P+D)
80-(45.5+36.1)
= Not determined due to oxidation

Wt% of residue, P = 58.8 wt%
Wt% of distillates, D = 45.1 wt%
Wt% of gas + losses, L = not determined

Input = Output
80g Residue + Distillates + Gas losses
(Sample) = 45.5g +36.1g + not determined
= 81.6g

3-3. Experiment 3

Synthesis of petroleum pitch from ethylene tar by simple distillation method under oxygen gas.

Material Balance:

Weight of empty reaction vessel 500ml (a) =139.0g
Weight of gas stripper (b) =24.3g
Weight of thermometer pocket (c) =18.4g
Total weight of reaction vessel
RV= a+b+c =181.7g

Amount of sample charged, SC =80g
Weight of sample charged and reaction vessel, A =SC+RV
=261.7g
Weight of receiver, R =152.0g
Weight of receiver and distillates (after 11hrs.),
B = R+D = 182.3g
Amount of residue and reaction vessel
C = P+RV =232.9g
Amount of pitch, P =C-RV
232.9-181.7 =51.2g
Amount of distillates, D = B-R
182.3-152.0 = 30.3g

Weight of gas + losses, L = SC-(P+D)
80-(51.2+30.3)
= Not determined
Wt% of residue, P = 58.5 wt%
Wt% of distillates, D = 42.6 wt%
Wt% of gas + losses, L = not determined

Input = Output
80g Residue + Distillates + Gas losses
(Sample) = 51.2g +30.3g + not determined
= 81.5g

3-4. Experiment 4

Synthesis of petroleum pitch from ethylene tar by using oxidizing catalyst such Acetic acid and Nitric acid in the presence of nitrogen gas.

Mixed the catalyst, 5g acetic acid and stirred it for 10 min then added 10 g nitric acid into ethylene tar, stirred it for 1hr.

Material Balance:

Weight of empty reaction vessel 500ml (a) =138.3g
Weight of gas stripper (b) =24.2g
Weight of thermometer pocket (c) =18.3g
Total weight of reaction vessel
RV= a+b+c =180.8g

Amount of sample charged, SC = Pyrolysis tar + Catalyst (Acetic acid+nitric acid)

75g+(5g+10g) =90g
Weight of sample charged and reaction vessel, A =SC+RV
=270.8g
Weight of receiver, R =197.4g
Weight of receiver and distillates (after 5hrs.),
B = R+D = 224.8g
Amount of residue and reaction vessel
C = P+RV =238.5g
Amount of pitch, P =C-RV
238.5-180.8 =57.7g
Amount of distillates, D = B-R
224.8-197.4 = 27.4g
Weight of gas +losses, L = SC-(P+D)
90-(57.7+27.4)
=4.9g

Wt% of residue, P = 64.1 wt%
Wt% of distillates, D = 30.4 wt%
Wt% of gas +losses, L = 5.4wt%

Input = Output
90g Residue + Distillates + Gas losses
(Sample) = 57.7g +27.4g + 4.9g
= 90g

3-5. Experiment 5

Synthesis of petroleum pitch from ethylene tar by simple distillation method in the presence of oxygen gas.

Procedure

Weighed the reaction vessel and receiver; charged the feedstocks (ethylene tar) weighing 80g into round bottom flask means reactor. The reactor was heated with a electric furnace and the temperature was monitored using a thermocouple.

The temperature of feedstocks raised to 200°C now allowed oxygen gas at a flow rate of 200ml/min into the reaction vessel through gas stripper, increased the temperature and set in the range of 350-450°C. This reaction takes place at atmospheric pressure. The drop of distillates entered the receiver at temp of 250°C. It has been observed that the rate of receiving the distillates was relatively high for the first five hours and later the distillates rate reduced.

The reaction was progressed for 8:30 hrs then empties the reaction vessel at 200°C into the glass bowl. It has been observed that some gasses are escaping with oxygen gas through the receiver by performing material balance of the feed and the distillates +residue.

This sample converted into a feasible mass type structure.

The residue from the flask was sent for the further analysis such as softening point determination, QI, TI, Coking value, beta resins.

The properties could not be finding for this sample.

Material Balance:

Weight of empty reaction vessel 500ml (a) =139.1g
Weight of gas stripper (b) =24.4g
Weight of thermometer pocket (c) =18.5g
Total weight of reaction vessel
RV= a+b+c =182.0g
Amount of sample charged, SC =80g
Weight of sample charged and reaction vessel, A =SC+RV
=262.0g

Weight of receiver, R =152.5g
Weight of receiver and distillates (after 8:30hrs.),
B = R+D = 186.6g
Amount of residue and reaction vessel
C = P+RV =240.5g
Amount of pitch, P =C-RV

240.5-182.0 =46.8g

Amount of distillates, D = B-R

186.6-152.5 = 34.1g

Weight of gas + losses, L = SC- (P+D)

80-(46.8+34.1)

=Not determined

Wt% of residue, P = 58.5 wt%

Wt% of distillates, D = 42.6 wt%

Wt% of gas + losses, L = Not determined

Input = Output

80g Residue + Distillates + Gas losses

(Sample) = 46.8g +34.1g + not determined

= 80.9g

3-6. Experiment 6

Synthesis of petroleum pitch from ethylene tar by simple distillation method in the presence of Air.

Procedure

Weighed the reaction vessel and receiver; charged the feedstocks (ethylene tar) weighing 80g into round bottom flask means reactor. The reactor was heated with an electric furnace and the temperature was monitored using a thermocouple.

The temperature of feedstocks raised to 200°C now allowed Air at a flow rate of 200ml/min into the reaction vessel through gas stripper, increased the temperature and set in the range of 350-450°C. This reaction takes place at atmospheric pressure. The drop of distillates entered the receiver at temp of 250°C. It has been observed that the rate of receiving the distillates was relatively high for the first five hours and later the distillates rate reduced.

The reaction was progressed for 12 hrs then empties the reaction vessel at 200°C into the glass bowl. It has been observed that some gasses are escaping with air through the receiver by performing material balance of the feed and the distillates +residue.

The residue from the flask was sent for the further analysis such as softening point determination, QI, TI, Coking value, beta resins.

Material Balance:

Weight of empty reaction vessel 500ml (a) =139.0g
Weight of gas stripper (b) =26.0g
Weight of thermometer pocket (c) =18.5g
Total weight of reaction vessel
RV= a+b+c =183.5g

Amount of sample charged, SC =80g
Weight of sample charged and reaction vessel, A =SC+RV
=263.5g
Weight of receiver, R =152.1g
Weight of receiver and distillates (after 12hrs.),
B = R+D = 180.8g
Amount of residue and reaction vessel
C = P+RV =225.2g
Amount of pitch, P =C-RV
225.2-183.5 =41.7g
Amount of distillates, D = B-R
180.8-152.1 = 28.7g

weight of gas+ losses, L = SC-(P+D)
80-(41.7+28.7)
=9.6g

Wt% of residue, P = 52.1 wt%
Wt% of distillates, D = 35.87 wt%
Wt% of gas+ losses, L = 12.0 wt%

Input = Output
80g Residue + Distillates + Gas losses
(Sample) = 41.7g +28.7g +9.6g
= 80g

3-7. Experiment 7

Synthesis of petroleum pitch from ethylene tar by simple distillation method in the presence of nitrogen gas.

The reaction was progressed for 14 hrs then empties the reaction vessel at 200°C into the glass bowl. It has been observed that some gasses are escaping with nitrogen through the receiver by performing material balance of the feed and the distillates +residue.

Material balance

Weight of empty reaction vessel 500ml (a) =154.3g
Weight of gas stripper (b) =24.4g
Weight of thermometer pocket (c) =22.1g
Total weight of reaction vessel
RV= a+b+c =200.8g
Amount of sample charged, SC =150g
Weight of sample charged and reaction vessel, A =SC+RV
150+200.8 =350.8g
Weight of receiver, R =152.1g
Weight of receiver and distillates (after 14hrs.),
B =R+D = 220.3g
Amount of residue and reaction vessel
C = P+RV =277.2g
Amount of pitch, P =C-RV
277.2-200.8 =76.4g
Amount of distillates, D = B-R
220.3-152.1 = 68.2g
weight of gas+ losses, L = SC-(P+D)
150-(76.4+68.2)
=5.4g

Wt% of residue, P = 50.9 wt%
Wt% of distillates, D = 45.5 wt%
Wt% of gas+ losses, L = 3.6 wt%

Input	= Output
150g	Residue + Distillates + Gas losses
(Sample)	= 76.4g +68.2g +5.4g
	= 150g

3-8. Experiment 8

Synthesis of petroleum pitch from ethylene tar by simple distillation method in the presence of nitrogen gas.

Procedure

Weighed the reaction vessel and receiver; charged the feedstocks (ethylene tar) weighing 270g into round bottom flask means reactor. The reactor was heated with a electric furnace and the temperature was monitored using a thermocouple.

The temperature of feedstocks rose to 200°C now allowed nitrogen at a flow rate of 200ml/min into the reaction vessel through gas stripper, increased the temperature and set in the range of 350-450°C. This reaction takes place at atmospheric pressure. The drop of distillates entered the receiver at temp of 250°C. It has been observed that the rate of receiving the distillates was relatively high for the first five hours and later the distillates rate reduced.

The reaction was progressed for 17 hrs then empties the reaction vessel at 200°C into the glass bowl. It has been observed that some gasses are escaping with nitrogen through the receiver by performing material balance of the feed and the distillates +residue.

The residue from the flask was sent for the further analysis such as softening point determination, QI, TI, Coking value, beta resins.

Material balance

Weight of empty reaction vessel 500ml (a) =200g
Weight of gas stripper (b) =30g
Weight of thermometer pocket (c) =20g
Total weight of reaction vessel
RV= a+b+c =250g

Amount of sample charged, SC =270g
Weight of sample charged and reaction vessel, A =SC+RV
250+270=520g
Weight of receiver, R =190g
Weight of receiver and distillates (after 17hrs.),
B =R+D = 340g
Amount of residue and reaction vessel
C = P+RV =350g
Amount of pitch, P =C-RV
350-250 =100g
Amount of distillates, D = B-R
340-190 = 150g

Weight of gas+ losses, L = SC- (P+D)

= 270-(100+150)
= 20g
Wt% of residue = 37.03 wt%
Wt% of distillates, D = 55.55 wt%
Wt% of gas+losses, L = 7.40 wt%

Input = Output
270g Residue + Distillates + Gas losses
(Sample) = 100g +150g +20g
= 270g

Chapter 4

Characterization (physicochemical properties) of Petroleum Pitches

Pitches samples prepared under different conditions were characterized for following properties

1. Softening Point
2. Quinoline Insoluble
3. Toluene Insoluble
4. Coking Value
5. Beta resins

The details for determining the above properties are given below in details.

4-1. Softening point

The softening point is defined as the temperature at which the softened sample in a standard softening point sample cup flows 20mm out of the 6.35mm opening on slow heating.

The softening point determination is suitable for substances, which soften on heating but do not have a low viscosity, such as pitches, bitumen, asphalts etc.

The measuring principle differs from that of the dropping point in respect to sample cup: it has an opening of 6.35mm.

Preparing the sample

Following ASTM D-3104 cut up pitch into 6---12mm pieces and melts about 25 ml of these in a 50ml beaker. The temperature must never ride more than 50°C above the expected softening point.

Start temperature

For exploratory measurement 5 min before the expected SP. For accurate measurement, 20-25°C below the expected softening point.

End temperature

The end point temperature usually corresponds to that of the measuring cell as the temperature program automatically stops as soon as the expected effect has appeared. With decomposition substance expected SP plus 20°C so that they are never overheated.

Preparing the method

To determine the SP of pitch we need a suitable method, which can be called up from the stored methods by entering the number in the main menu or by selection from the method list.

Define operating mode, softening point (F1 MODE, F2SOFTEN)

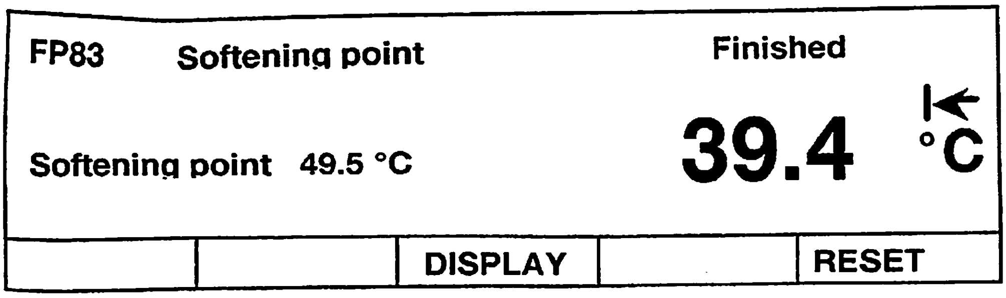
Enter temp program. Start temp 30°C, heating rate 2°C/min.
Starting the measurement

As soon as we have selected or entered a method

1. Press key or F1 RUN respectively.
2. Enter sample identification
3. Insert sample
4. Start determination with F1 RUN

Results

As soon as the softening point has been determined or the end point temp has been reached the result of the measurement appears



FP83 **Softening point** **Finished**

Softening point 49.5 °C **39.4 °C**

| | | DISPLAY | | RESET |

When the measurement is complete, the result appears. The status display above „ °C" shows that the measuring cell is being cooled to the start temperature.

Table1

Softening point for different types of samples

Experiment	Condition	Reaction duration hrs	Softening points ^{0}C
1	Nitrogen	5:00	78
2	Air	5:00	138
3	Oxygen	5:00	195
4	Catalyst (Acetic Acid + Nitric Acid)+ nitrogen	5:00	200
5	Oxygen	8:30	Not determined
6	Air	12:00	130
7	Nitrogen	14:00	123
8	Nitrogen	17:00	202

Fig 1 has been plotted for the softening point at constant reaction duration, for four types of samples under different conditions.

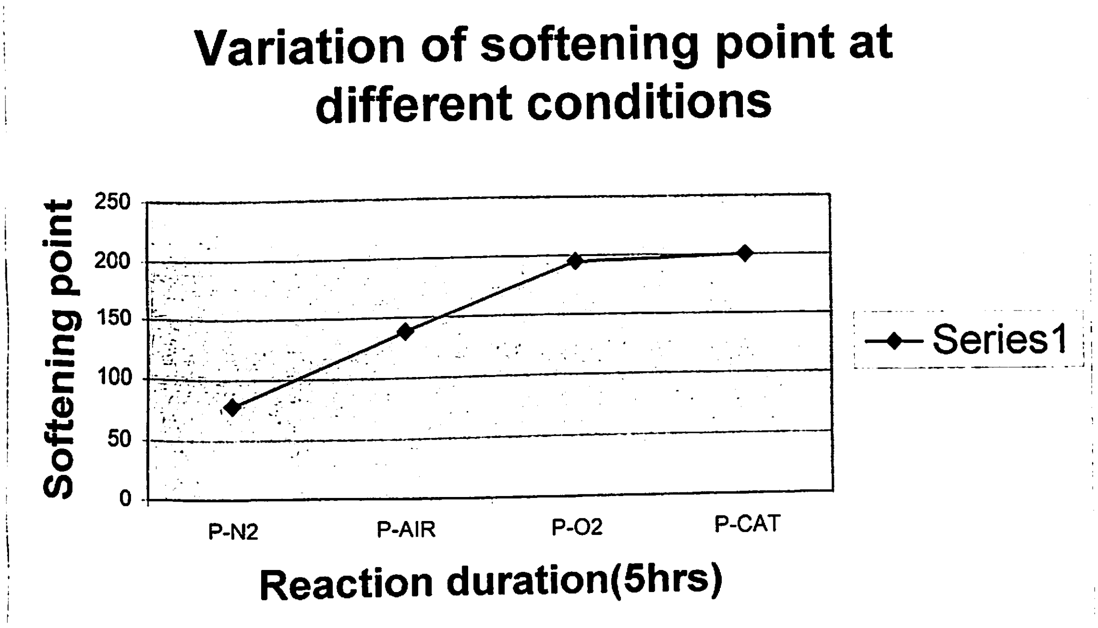


Fig. 1

4-2. Quinoline Insolubles

This standard is issued under the fixed operation D-2318

The principal of the determination of QI in pitch involves digesting the sample in quinoline to decrease its viscosity and filtering the solution. The insoluble material is washed, dried and weighed.

Because the filtration is performed according to ASTM procedure by vacuum filtration. This test method covers the determination of QI matter in Pitch.

Analysis of the isolated QI is often required for better characterization, evaluation of QI by scanning microscopy.
Preparation of working sample

Crushed sample to pass a 250µm screen but so they are retained on a 159µm screen. Remove pitch from 150µm screen by a brush. Crushing can be done with a small jaw crusher or a mortar and pestle; no particle in the representative sample should be larger than 5mm in any dimensions.

Procedure

Took one g of crushed pitch sample taken in a one neck round bottom flask of 250ml; added 25 ml distilled Quinoline into the same flask.

Reflux the contents for half an hour and filtered the contents by using the G4 funnel connected to a vacuum pump.

Used 10 ml of distilled quinoline to clear the contents in the flask, three times. Dried the funnel for half an hour in an oven, weighed the contents along with theG4 funnel.

The concentration of Quinoline Insoluble determined by using the following equation

$$QI\ (wt\ \%) = (W3-W2/W1) \times 100$$

Where,
W1- weight of the sample
W2- weight of the empty funnel
W3- weight of funnel with QI

Table 2
Quinoline Insolubles for different types of samples

Experiment	Condition	Reaction duration hrs	Quinoline insolubles
1	Nitrogen	5:00	3.5
2	Air	5:00	9.3
3	Oxygen	5:00	11.1
4	Catalyst (Acetic Acid + Nitric Acid)+ nitrogen	5:00	6.4
5	Oxygen	8:30	Not determined
6	Air	12:00	3.5
7	Nitrogen	14:00	5.3
8	Nitrogen	17:00	1.9

Fig 2 has been plotted for the quinoline insoluble at constant reaction duration, for four types of samples under different conditions

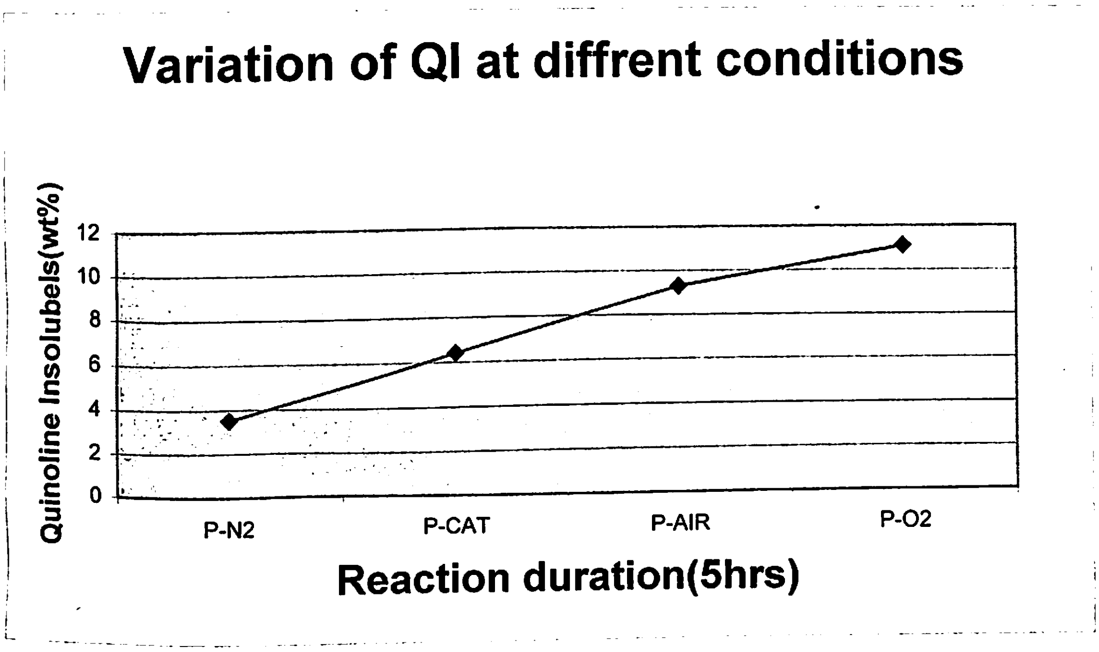


Fig .2

4-3. Toluene insolubles

Standard test method for TI content in petroleum pitch.

This standard is issued under the fixed operation D-4312.

This test method covers the determination of toluene insoluble matter TI in pitch.
This test method is useful for evaluating and characterization of pitch is one element in establishing the uniformity of shipment of sources of supply.

Preparation of working sample

Crush sample to pass a 250μm screen but so they are retained on a 159μm screen. Remove pitch from 150μm screen by a brush. Crushing can be done with a small jaw crusher or a mortar and pestle; no particle in the representative sample should be larger than 5mm in any dimensions.

Procedure

Took one g of crushed pitch sample taken in a one neck round bottom flask of 250ml; add 25 ml Toluene (Sulfur free) into the same flask.

Reflux the contents for half an hour and filtered the contents by using the G4 funnel connected to a vacuum pump.

Use 10 ml of Toluene (Sulfur free) to clear the contents in the flask, three times. Dried the funnel for half an hour in an oven, weighed the contents along with theG4 funnel.

The concentration of Toluene Insoluble by using the following equation

TI (wt %) = (W3-W2/W1) ×100
Where
W1- weight of the sample
W2- weight of the empty funnel
W3- weight of funnel with TI

Table 3

Toluene Insoluble for different types of samples

Experiment	Condition	Reaction duration hrs	Toluene in soluble
1	Nitrogen	5:00	18
2	Air	5:00	35.2
3	Oxygen	5:00	48
4	Catalyst (Acetic Acid + Nitric Acid)+ nitrogen	5:00	49.8
5	Oxygen	8:30	Not determined
6	Air	12:00	29
7	Nitrogen	14:00	11
8	Nitrogen	17:00	18

Fig 3 has been plotted for the Toluene insoluble at constant reaction duration, for four types of samples under different conditions

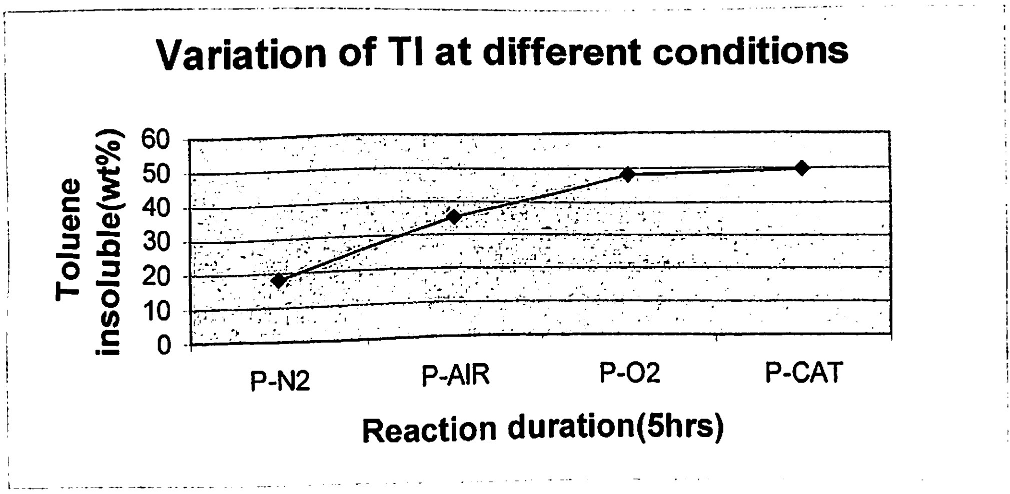


Fig .3

4-4. Coking value

Coking value determined by using micro carbon residue Tester Model ACR- M3 by TANAAK SCIENTIFIC LIMITED

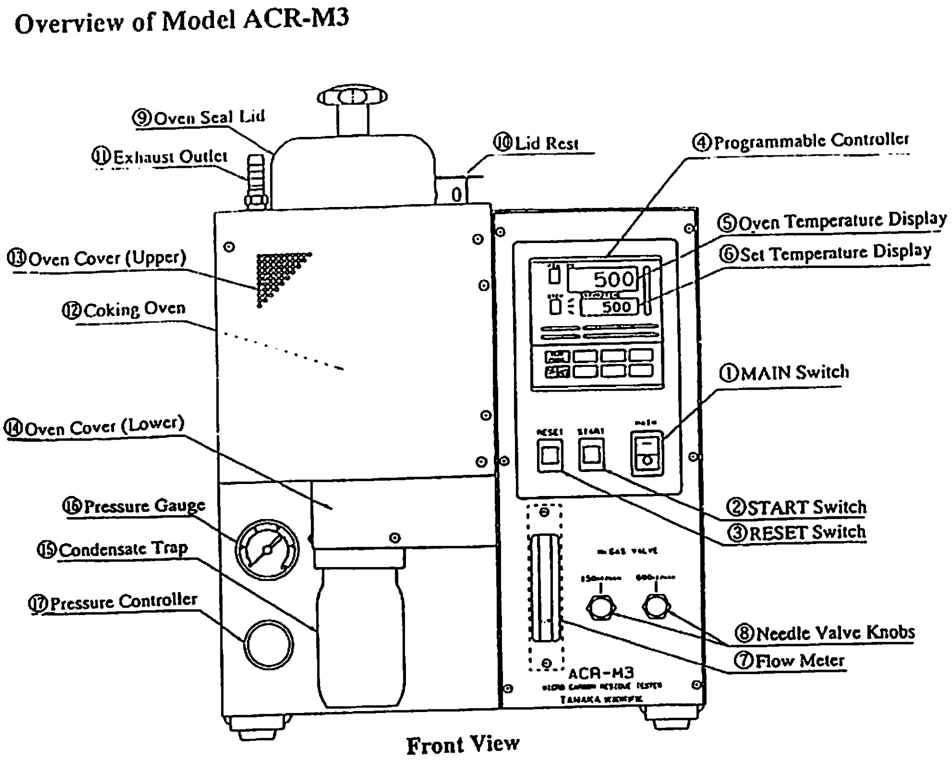


Fig – overview of model ACR-M3

Operation

Turned the main switch on. Adjusted pressure controller for nitrogen gas pressure gauge indicates 150kPa. This gas was used as an inert carrier gas.

The nitrogen gas should flow through the oven at 150ml/min. if the flow rate was not 150ml/min, adjusted it accordingly with N2 needle valve for 150ml/min.

Measured the sample into a sample vial. There were three kinds of sample vials, large, small and medium. Normally used small vials.

The sample size to be measured is as below

Obtained weight of clean sample vials and record the mass to nearest 0.1 mg.

During weighing and filling, handle vials with forceps to help minimize weighing errors.

Transferred an appropriate weight of sample into a tarred sample vial, reweighing to nearest 0.1 mg and record.

Placed the load sample vials into vial holder.

The flow rate of nitrogen increased to 600ml/min automatically for the first 10 min after pressing the start switch. If the flow rate was not 600ml/min, adjusted N2 needle valve for 600ml/min.

When oven temp was less than 250°C, placed the lid to the lid rest to cool down and removed the vial holder-using hook for further cooling in desiccator.
Final weighing

Transferred sample vials to desiccator and allow vials to cool to room temp. Weighed the cool vials to the nearest 0.1mg and record.

Perform appropriate calculations with weight found, % residue is the weight of final vial dived by weight of original vial with sample.

Coking value can also be determined by this formula

C.V. of Pitch = 16.4+0.517(%QI) +0.31 (S.P.°C)

Table 4
Coking value for different types of samples by formula

Experiment	Condition	Reaction duration hrs	Coking value
1	Nitrogen	5:00	42.3
2	Air	5:00	63.9
3	Oxygen	5:00	82.5
4	Catalyst (Acetic Acid + Nitric Acid)+ nitrogen	5:00	81.7
5	Oxygen	8:30	Not determined
6	Air	12:00	58.5
7	Nitrogen	14:00	57.2
8	Nitrogen	17:00	80

Fig 4 has been plotted for the Coking value at constant reaction duration, for four types of samples under different conditions

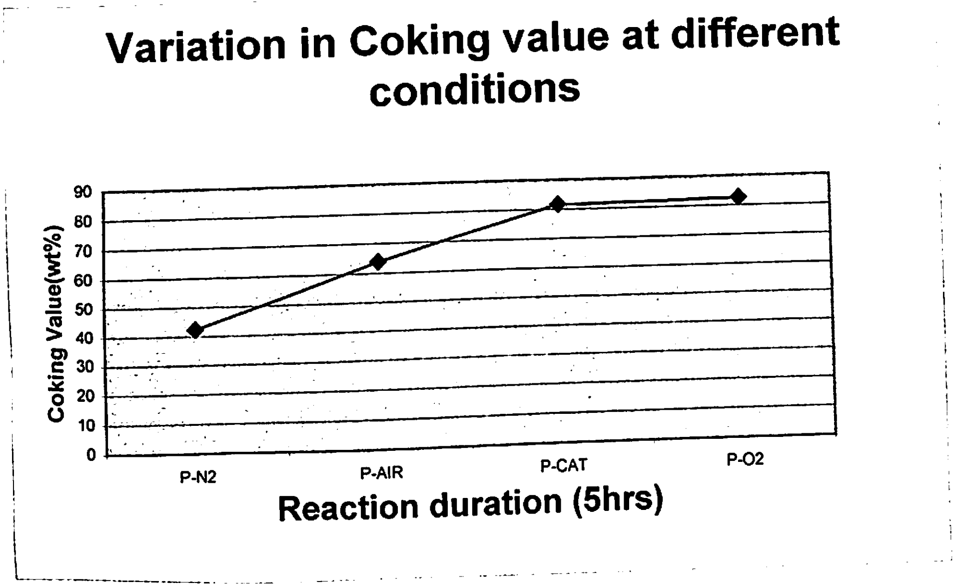


Fig. 4

4-5. Beta Resin

Beta resin is the mathematical difference between toluene insoluble and quinoline insoluble and represents a large polynuclear molecular weight portion in pitch.

Beta resin means quinoline soluble but toluene nonsoluble.

$$\beta\text{- Resin} = TI\text{-}QI$$

Table 5
Beta resins for different types of samples by formula

Experiment	Condition	Reaction duration hrs	β - Resin = TI-QI
1	Nitrogen	5:00	14.5
2	Air	5:00	25.9
3	Oxygen	5:00	36.9
4	Catalyst (Acetic Acid + Nitric Acid)+ nitrogen	5:00	43.4
5	Oxygen	8:30	Not determined
6	Air	12:00	25.5
7	Nitrogen	14:00	5.7
8	Nitrogen	17:00	16.1

Fig 5 has been plotted for the beta resins at constant reaction duration, for four types of samples under different conditions

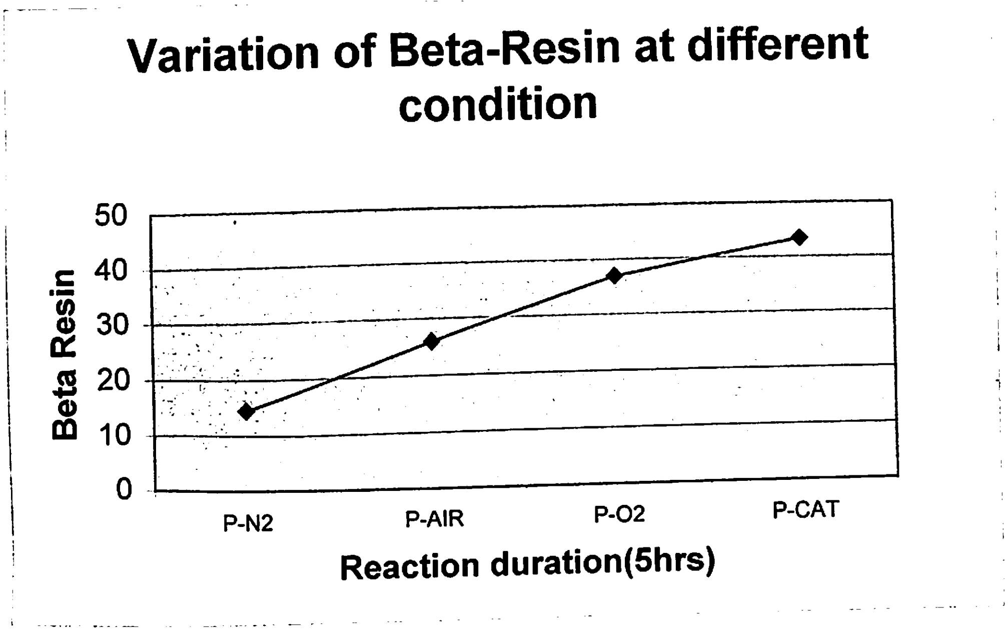


Fig. 5

Chapter-5

RESULTS AND DISCUSSIONS

Pitch synthesized by oxidative and non-oxidative routes have been characterized for their physiochemical properties for their commercial significance. The results obtained by characterization are as follows

1. Softening point is defined as the temp at which the softened sample in a standard cup flows 20mm out of the 6.35mm opening on slow heating.
Significance of softening point determination is suitable for substance, which soften on heating.

The softening point of the pitches synthesized under oxidative and Nonoxidative conditions are shown in Table1 and Graph1.

It has been observed that the softening point of the sample synthesized in the presence of nitrogen and a duration of 5:00hrs has been 78°C and for the same condition when the duration is increased from 5hrs to 14hrs. S.P. has come down to 123°C. Again for the same condition duration is increased from 14hrs to 17hrs, S.P. has increased to 202°C.

This is due to the occurrence of polycondensation reaction and formation of more aromatic complexes.

Also for the sample prepared under oxidative conditions with air, It has been observed that softening point of the pitches synthesized for duration of 5hrs has been 138°C and for the same condition when the duration is increased from 5 to 12hrs, softening point is decreased to130°C.

With oxygen it has been observed that softening point of the oxidized pitches synthesized for duration of 5hrs, softening point has been 195°C due to the cross-linking and weight gain also occurred.

For the same condition when the duration is increased from 5hrs to 8:30hrs, softening point could not be determined because it has been converted into a different type of sample.
In the presence of the catalyst, softening point of pitch synthesized for duration of 5hrs softening point has been 200°C.

It has been observed for this condition, we got high softening point and also increased molecular weight of the sample.

1) **Quinoline Insolubles** in wt% of the pitches synthesized under oxidative and Nonoxidative conditions are shown in Table2 and Graph2.

It has been observed that the QI value for the sample synthesized in the presence of nitrogen and a duration of 5hrs, 14hrs, 17hrs have been 3.5wt%, 5.3wt%, and 1.9wt%

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Sample prepared under oxidative condition conditions with air, it has been observed that the QI of the pitches synthesized for a duration of 5hrs and 12hrs have been 9.3wt% and 3.5wt%

When sample prepared under oxidative condition with O_2, it has been observed that the QI of the pitches synthesized for a duration of 5hrs and 8:30 hrs, for 5 hrs treated pitch, QI has been 9.3wt% and QI value could not be determined for 8:30hrs treated pitch
When the sample prepared with catalyst for duration of 5hrs QI has been 6.4wt%.

High QI indicate that the product of incomplete combustion (carbon black and thermal black) high compare to low QI.

2) **Toluene Insolubles** in wt% of the pitches synthesized under oxidative and Nonoxidative conditions are shown in Table3 and Graph3.

It has been observed that the TI value for the sample synthesized in the presence of nitrogen and a duration of 5hrs, 14hrs, 17hrs have been 18wt%, 11wt%, and 18wt%.

Sample prepared under oxidative condition conditions with air, it has been observed that the TI of the pitches synthesized for a duration of 5hrs and 12hrs have been 35.2wt% and 29wt%

When sample prepared under oxidative condition with O_2, it has been observed that the TI of the pitches synthesized for a duration of 5hrs and 8:30hrs, for 5 hrs treated pitch, TI has been 48wt% the TI value could not be determined for 8:30hrs treated pitch.

When the sample prepared with catalyst for duration of 5hrs TI has been 49.8wt%.

3) **Coking value** in wt% of the pitches synthesized under oxidative and Nonoxidative conditions is shown in Table4 and Graph4.

It has been observed that the coking value for the sample synthesized in the presence of nitrogen and a duration of 5hrs, 14hrs, 17hrs have been 42.3wt%, 57.2wt%, and 80wt%.

Sample prepared under oxidative condition conditions with air, it has been observed that the coking value of the pitches synthesized for a duration of 5hrs and 12hrs have been 63.9wt% and 58.5wt%

When sample prepared under oxidative condition with O_2, it has been observed that the coking value of the pitches synthesized for a duration of 5hrs and 8:30hrs, for 5 hrs treated pitch, coking value has been 82.5wt% and the coking value could not be determined for 8:30hrs treated pitch.

When the sample prepared with catalyst for duration of 5hrs CV has been 49.8wt%.

Oxygen treated sample contains high CV compare to others. High CV indicates that high carbon content.

4) **Beta resin** in wt% of the pitches synthesized under oxidative and Nonoxidative conditions are shown in Table5 and Graph5.

It has been observed that the β-Resins for the sample synthesized in the presence of nitrogen and duration of 5hrs, 14hrs, and 17hrs have been 14.5wt%, 5.7wt%, and 16.1 wt%.

Sample prepared under oxidative condition conditions with air, it has been observed that the β-R of the pitches synthesized for a duration of 5hrs and 12hrs have been 25.9wt% and 25.5wt%.

When sample prepared under oxidative condition with O_2, it has been observed that the β-Resins of the pitches synthesized for a duration of 5hrs and 8:30hrs, for 5 hrs treated pitch, β-Resin has been 36.9wt% and the β-Resin value could not be determined for 8:30hrs treated pitch
When the sample prepared with catalyst for duration of 5hrs β-Resin has been 43.4wt%.

High β-Resin indicates that a large polynuclear weight portion in pitch.

CONCLUSION

It has been observed that as thermal soaking period is increased, the physiochemical properties like softening point, quinoline insoluble and coking value of pitches are increased.

It has also observed that for same residence period (5hrs) the increase in softening point and soaking value is more in case of oxygen purging as compared to nitrogen purging.

It has been further observed that preparation of pitches in presence of liquid oxidizing agent is most effective way to increase softening point and coking value. The main drawback of this method is some traces of catalyst may remain in the pitches itself, which may affect the end product quality.

Preparation of pitches in atmospheric air is most effective way to increase the softening point and coking value. Such type of pitches is suitable for making carbon fibres and activated carbon spheres. Since in air, oxygen contents are less compared to pure oxygen. The pitches properties are easily controllable.

REFERENCES

Manoj Seivastava, Himmat Singh and T.S.R.Prasada Rao, Production of high value industrial carbon materials from refinery/ petrochemical feedstocks, Hydrocarbon technology, June 1999, Issue no. 49

Robert H. Wombles, Developing Coal tar/ Petroleum pitches, Kopperes industries ltd.

John R. Kershaw and Krista J.T.Black, structural characterizationof coal tar and petroleum pitches, Energy &Fuels 1993,7, 420-425.

Yolanda Martin, Roberto Garcia, Pat Keating, Colin E.Snape and Sabino R. Moinelo, A study of polymerization and condensation reaction during the heat treatment under gas blowing conditions, Energy& Fuels 2000,14,380-382.

A.Stocks, Vincenr J.Guercio, feedstocks for carbon black, needle coke and electrode pitch.

G.N.Mathur, V.S. Tripathi, T.L.Dhami, O.P. Bhal, Indo Carbon 2003.

J.DR Bohlav and W.T.K Stevens, The oxidative stabilization and carbonization of a synthetic mesophase pitch, Carbon, vol 33, No 5, page 693-711, 1995

Chiharv Yamnguchi, Juji Mondori, Akira Matsumoto, Hidekazu Honma, Haruo Kumagai and Yuzo Sanda, Air blowingreactions of pitch, Carbon, vol. 33, No.2, page 193-201,1995.

J. H. Choi, H.Kumagai, T.Chiba and Y.Sanada, Carbonization of pitches in air blowing batch reactor, carbon, vol.33, No.2, page 109-114, 1995

A.Dominguez, C.Blanco, R.Santamaria, M.Granda,C.G. Blanco, R. Menendez, monitoring of coal tar pitch composition changes during air blowing by gas chromatography, JO Chromatography A, 1026(2004) 231-238.

J.DR Bohlav and W.T.K Stevens, The oxidative stabilization and carbonization of a synthetic mesophase pitch part II, Carbon, vol 33, No 5, page 713-731, 1995

Th. Metzinger and K.J. Huttinger, investigation on the crosslinking of binder pitch matrix of carbon bodies with molecular oxygen, carbon vol.35, No 7, page 885-889, 1997.

L. Singer and S. Mitchell, Diffusion of oxygen into pitch, carbon, vol 35 no5, page599-604, 1997

E. Vilaplana ortego, J.Alcaniz monge, D.Cazorla-Amorous, Stabilization of low softening point petroleum pitch fibre by HNO3, carbon, vol 41, No. 2, page 1001-1007, 2003.

Manual of Mettler Toledo for the determination of softening point

G. R.Ramovacck, The determination of the QI content of pitch, Science and Tech. Center, Koppers company, inc.

Standard test method for QI content of Tar and pitch, annual Book of ASTM standards, vol.05.02.

Standard test method for TI content of Tar and pitch, annual Book of ASTM standards, vol.05.01.

Manual Tester Model ACR- M3 for determination of coking value.

Mustafa Z. Ozel (University of Pamukkale), Keith D. Bartle (University of Leeds), Production of Mesophase pitch from coal tar and petroleum pitches using supercritical fluid extraction.

Robert H. wombles, Development of binder pitches from coal extract and coal tar pitch blends, Koppers industries.

O. P. Bhal, G.Bhatia, R.B.Mathur, R. K.Aggarwal, Newer carbon products, oct 9-10-1992.

O. P. Bhal, G.Bhatia, R.B.Mathur, R. K.Aggarwal, pitch and pitch based products Nov. 24-25, 1989, National Physical lab.