American Journal of Chemical and Biochemical Engineering
2021; 5(2): 55-60
http://www.sciencepublishinggroup.com/j/ajcbe
doi: 10.11648/j.ajcbe.20210502.13
ISSN: 2639-9970 (Print); ISSN: 2639-9989 (Online)

Effect of Process Parameter on Coal Tar Distillate Products

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To cite this article:
Ajay Kumar Gupta, Subhadra Sen, Ritesh Kumar, RV Ramna, Sarita Kumari Sanjay Dhakate. Effect of Process Parameter on Coal Tar Distillate Products. *American Journal of Chemical and Biochemical Engineering.* Vol. 5, No. 2, 2021, pp. 55-60.
doi: 10.11648/j.ajcbe.20210502.13

Received: June 29, 2021; **Accepted**: July 22, 2021; **Published**: October 12, 2021

Abstract: Coal tar pitch is broadly classified into two kinds based on their properties: Binder Pitch for aluminum and Graphite Industry Impregnated Pitch with less than 0.5% QI (Quinoline Insoluble) used in the graphite industry. To maximize value realization through downstream processing of coal tar, proposal was made to explore the feasibility of conversion of different qualities of coal tars from different steel plants to coal tar pitch (CTP) of different varieties (binder as well as zero QI impregnated for both Al & graphite industries), through first level of fractional distillation. In this study, four qualities of coal tar samples three from plant 1 (TP-1, TP-2, and TP-3) and one from plant 2 (TP-4) were collected and sent to laboratory for necessary evaluation, conversion and subsequent characterization studies. Zero QI impregnated pitch from coal tar (TP-1, TP-2, and TP-3) can also be made using solvent extraction or sedimentation process, which may not be cost-effective. Depending on the required specifications for binder & impregnated grade pitches, process parameters during vacuum distillation, were optimized through this collaborative work. On conversion of coal tar sample into coal tar pitches, QI content depends on distillation temperature, vacuum and soaking time.

Keywords: Coaltar, Pitch, Distillation, Byproduct

1. Introduction

Coal tar is obtained as a by-product in the destructive distillation of metallurgical coal carried out by the steel industry. Coal tars contains phenols, polycyclic aromatic hydrocarbons (PAHs), and heterocyclic compounds. [1]

The fraction which contains 3-5 ring aromatic ring PAHs, are escaped from polymerization in conventional thermal treatments at atmospheric pressure. It required a special kind of treatment involves thermal oxidative condensation and subsequent thermal treatment and distillation until the pitch reaches the desired softening point. [2]

This tar also contains soot–like fine particles formed by the thermal cracking of tar vapors in coke ovens and their amount depends on various process parameters, battery conditions and quality of coal. These fine particles are insoluble in strong solvent like quinoline, and is termed as quinoline insoluble (QI) [3]. By thermal treatment, QI present in coal tar or coal tar pitch are converted into called mesophase. The mesophase content of coal tar or coal tar pitch is determined by a test method designated as ASTM D 4616. [4]

Since coal tar pitches (CTP) are obtained from fractional distillation of coal tar as residue, so these fine QI particles are also found in pitches. Based on the amount of QI content, pitches can be of two types: binder pitch and impregnating pitch. The quinoline insoluble contents for the binder grade pitch usually lie in the range of 5-18% depending upon the application and for impregnating pitch this value is very low, 0-1%. Chemically, coal tar pitch is a complex mixture of many predominantly aromatic hydrocarbons made up of several fused benzene rings, their alkyl and hydroxyl derivatives, and the corresponding heterocyclic compounds containing oxygen, nitrogen or sulphur.

By TG analysis, it is seen that the significant difference of the volatilities of coal tar pitch samples which is consistent with their different softening point. Particularly, the more volatile coal tar pitch is the electrode binder featured by the

much lower softening point [7].

Fractionalized distillation is an effective method to manipulate the paraffinicity of an aliphatic-rich solvent, enhancing QI-removing performance. [10]

Temperature and thermal treatment duration are play a critical role on the microstructures formation. The thermal treatment at a lower temperature and shorter duration are promotes the MCMBs formation. [11]

Now days another method of extraction to be developed i.e. supercritical fluid extraction (SFE). In this process, the values of significant properties of supercritical fluids (SFs) such as density, diffusivity, viscosity, etc. are used to explore the advantages of more expeditious and efficient extractions. [12]

These Coal-tar pitches have been employed for more than a century in many industrial processes. Although the main application of pitch is as a binder in aluminium and graphite technology, in recent years coal-tar pitches have been increasingly used as advanced carbon precursors because they are regarded as one of the most economical and abundant sources of carbon [5].

2. Experimental Work

Four coal tar samples of different qualities were collected from Steel plants and send to laboratory for necessary test work, as given below. The marking of samples is done as drum 1, drum 2, drum 3 and drum 4. First, coaltar sample has characterized in terms of QI & TI contents, Coking value, ash content etc. [8, 9]. Than the conversion of Coal tar samples in to different grades of binder and impregnated pitches for the application in Aluminium & Graphite Industries. Finally, characterization of CTP has completed in terms of softening point, QI & TI contents, coking value, ash & moisture contents etc. Another method to determine the analysis of coal tar pitch and its thermal reaction is also developed i.e. Laser Desorption Ionization Mass Spectrometry, mass spectrometry, electron ionization, chemical ionization and liquid ionization etc. [13]

3. Characterization of Four Samples of Coal Tar

The characteristics of four different coal tar samples are shown in Table 1. There are two main types of Quinoline insoluble (QI): primary and secondary QI, the primary QI contains solid soot like particles produced in the metallurgical coke oven or can be formed from incomplete combustion of coal volatiles and it can be due to the impurities present in the coal. The secondary QI is generated during the processing and depends on process conditions due to polymerization and condensation reactions which increase the solid content of the pitch. The primary QI content varies from 5% to 0.5%. Similarly, Toluene insoluble (TI) content varies from 10% to 5%.

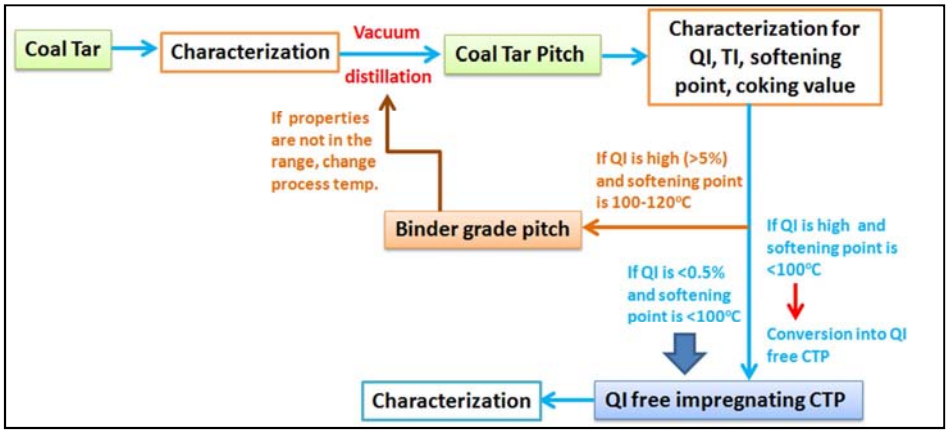

Figure 1. *Schematic diagram for coal tar pitch.*

Table 1. *Properties of Coal Tar Samples.*

Properties	Coal Tar Samples			
	Drum 1	Drum 2	Drum 3	Drum 4
Quinoline insoluble (%)	5.14±0.35	3.58±0.25	2.8±0.2	0.33±0.1
Toluene insoluble (%)	10±1	7.5±0.8	4.5±0.4	3.34±0.5
Coking value (%) at 950°C	24±0.7	20±0.7	25±0.6	18±0.8
Coking value (%) at1000°C	23.2±0.6	19.5±0.5	24.3±0.3	17.4±0.4
Ash content (%)	0.18	0.15	0.1	0.02
Density (g/cc)	1.14±0.01	1.13±0.01	1.11±0.01	1.11±0.01
Kinematic viscosity at 100°C in Cst	14.14	9.34	7.03	6.45
Pour point (°C)	-3 to -2	-3 to -2	-3 to -2	-3 to -2
Flash Point (°C)	150-154	140-145	135-138	132-136
CH ratio	10.24	10.05	9.69	9.69
BMCI	>50	>50	>50	>50

4. Conversion of Coal Tar into Coal Tar Pitch (CTP)

As already mentioned that coal tar is a complex mixture of hydrocarbons with wide range of molecular weights, so to convert coal tar into coal tar pitch, lower molecular weight hydrocarbons need to be removed from the coal tar. Here, a vacuum distillation assembly was used for converting coal tar into coal tar pitch. For synthesis of coal tar pitch from coal tar, an experimental set-up (Figure 2) made of borosilicate glass for distillation of coal tar was designed and developed and used for preparing the coal tar pitch. For this, four samples of coal tar were distilled at different temperatures with the help of temperature controller in distillation assembly under reduce pressure to obtain coal tar pitch as residue. Volatiles coming out from the coal tars were condensed through condenser and collected in receiving flask. This was the feasibility study to convert coal tar into coal tar pitch. The so obtained coal tar pitch was characterized for various parameters as mentioned above.

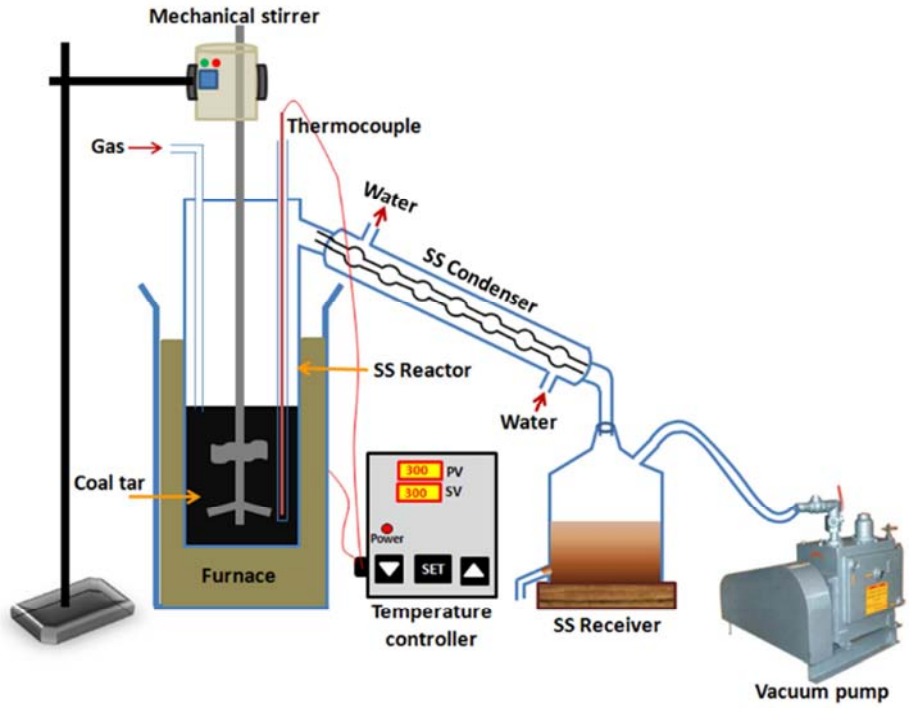

Figure 2. *Distillation assembly for synthesis of coal tar pitch.*

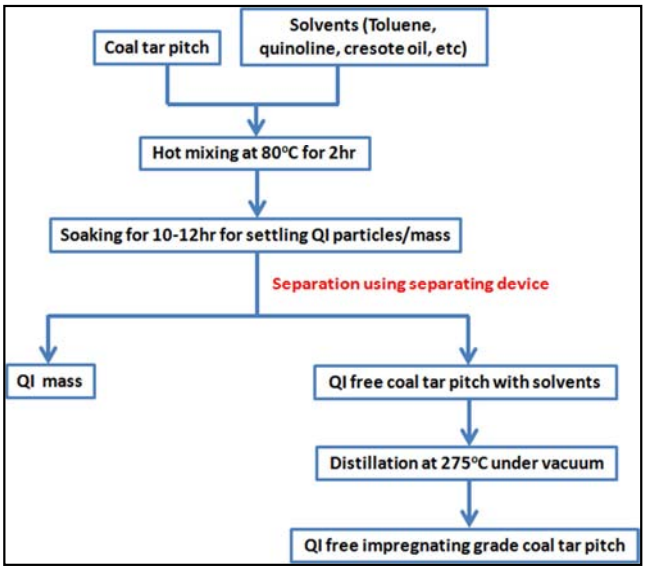

Figure 3. *Flow diagram of the process for making QI free coal tar pitch.*

5. Conversion of Coal Tar to Coal Tar Pitch Samples

Experiments were carried out to prepare binder grade coal tar pitch from distillation of coal tar of Drum 1, Drum 2, Drum 3 and Drum 4. It was observed that softening point of pitches increases with increase in distillation temperature. The increase in softening point of coal tar pitches with temperature is due to the removal of lower molecular weight species and to the polymerization and condensation reactions taking place in the pitch. The higher QI content for coal tar as compared to source coal tar samples are actually mesophase (in small amount) developed during heat treatment process due to increase in molecular weight as solubility depends on largely on molecular weight and to a lesser on the structure. Similarly, TI & coking value is also increased in the samples treated at different temperatures. This is because lower molecular weight species escape as volatiles and the carbon yield of the pitch increases. It was observed that the yield of coal tar pitch was continuously

decreasing with increase in temperature due to the increase in removal of volatiles from a level of 50% to 40%.

The flow diagram for making QI free pitch is presented in Figure 3. The properties of binder grade CTPs and impregnating grade CTPs are shown in Table 2 below.

Coal tar samples from Drum 1 & Drum 2 are suitable for production of binder grade coal tar pitches which can be used by different graphite/aluminum industries as binder. Similarly, Coal tar samples from Drum 3 and Drum 4 are suitable for the production of impregnated grade of pitch. Several qualities of coal tar pitch samples were prepared (both binder as well as impregnated grades), based on the requirements from Aluminium & Graphite industries, from all coal tar samples by varying the distillation temperature and vacuum. Coal tar samples from Drum 1 & Drum 2 can also be used for making impregnating grade coal tar pitch after reducing QI content by sedimentation process.

6. Characterization of Coal Tar Pitch Samples

Metals present in coal tar pitch can be determined using energy dispersive X-ray spectroscopy (EDS) attached in a FESEM. It gives an idea about the elements present in a particular area. Figure 4 shows FESEM image of coal tar pitch made from Drum 1 & Drum 4, it can be seen that the surface of coal tar pitch is smooth with some pores and voids. EDS of CTP samples produced from Drum 1 & Drum 4 are shown in Figure 5 with elements present in the sample.

Table 2. *Consolidated Table on CTP characteristics.*

Properties	**Different coal tar samples**				
	(Drum 1)	**(Drum 1)**	**(Drum 2)**	**(Drum 3)**	**(Drum 4)**
Expected Pitch	**Al-grade binder Pitch**	**Impregnating Pitch**	**Graphite grade binder Pitch**	**Al-grade binder Pitch**	**Impregnating -grade Pitch**
Softening point (°C)	116±1	88	99±1	109±1	87±1
Quinoline Insoluble (%)	9.65±0.2	0.53	11.1±0.5	6.7±0.4	0.72±0.02
Toluene Insoluble (%)	30.8±1.2	22.3	24.0±0.8	27.0±0.8	10.28±0.3
Coking value (%)	56.1±0.6	43.2	50.7±0.4	55.4±0.7	40.0±0.4
Ash content (%)	<0.2	~0.05	<0.16	<0.12	<0.05
Moisture content (%)	<0.5%	<0.5%	<0.5	<0.5	<0.5
Flash point (°C)	>260	242	>250	--	~235
Density (g/cc)	1.27	1.1	1.26	1.28	1.17
Specific gravity	1.32	1.28	1.29	1.30	1.26
Viscosity at 180°C in cP	725	125	225	350	100
Remarks	Further controlling the processing parameters such as temperature, residual time and vacuum level, properties can be tailored according to customer requirements. The QI content of the samples was tried to reduce by sedimentation process.				

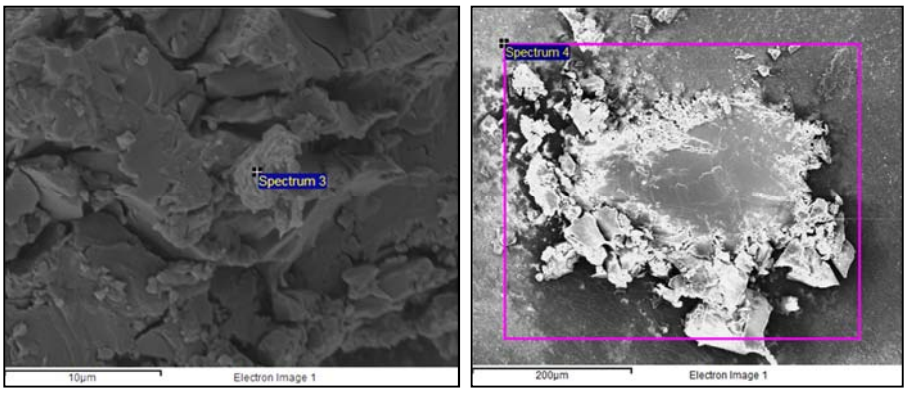

Figure 4. *FESEM image of coal tar pitch.*

TGA result obtained for coal tar pitch samples presented in Figure 6, shows that around 10% weight loss occurs at 100°C and up to 15% to 20% of residue is obtained after 1000°C. It can also be seen that major weight loss 95% to 33% due to removal of volatile takes place between temperatures from 150 to 450°C. After 500°C, the weight of carbon residue decreases to an insignificant amount. The thermal behaviour of the pitches are correlated with their softening points, whereas it is not correlated with the elemental composition, namely the hydrogen and carbon content of pitches. [6]

Table 3. *Elements present in coal tar pitch.*

Drum 1			**Drum 4**		
Elements	**Weight%**	**Atomic%**	**Elements**	**Weight%**	**Atomic%**
Carbon, C	46.51	56.94	Carbon, C	84.25	86.68
Nitrogen, N	8.85	9.29	Nitrogen, N	9.42	8.33
Oxygen, O	28.9	26.56	Oxygen, O	6.07	4.7
Sodium, Na	1.61	1.03	Sodium, Na	0.05	0.03
Aluminum, Al	2.34	1.27	Copper, Cu	0.07	0.01
Silicon, Si	6.95	3.64	Calcium, Ca	0.13	0.04
Iron, Fe	4.53	1.19			
Cobalt, Co	0.31	0.08			

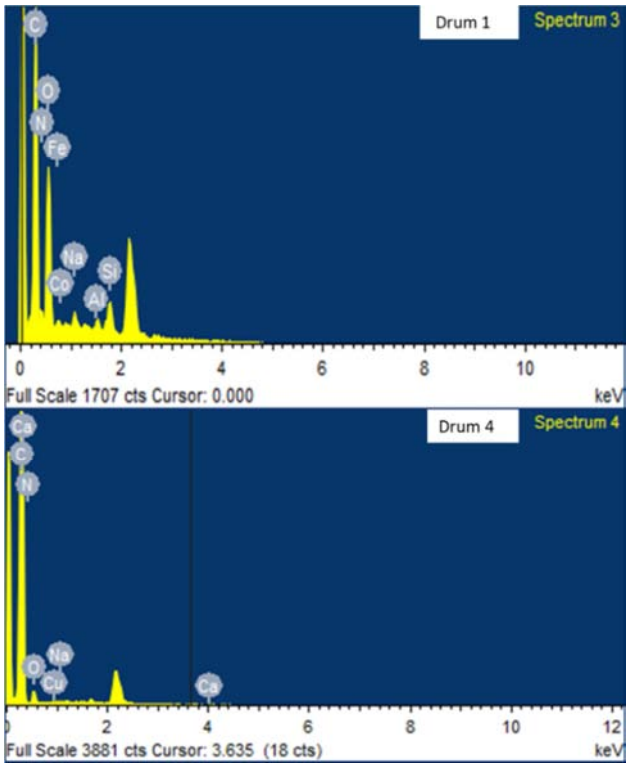

Figure 5. *EDS of coal tar pitch samples.*

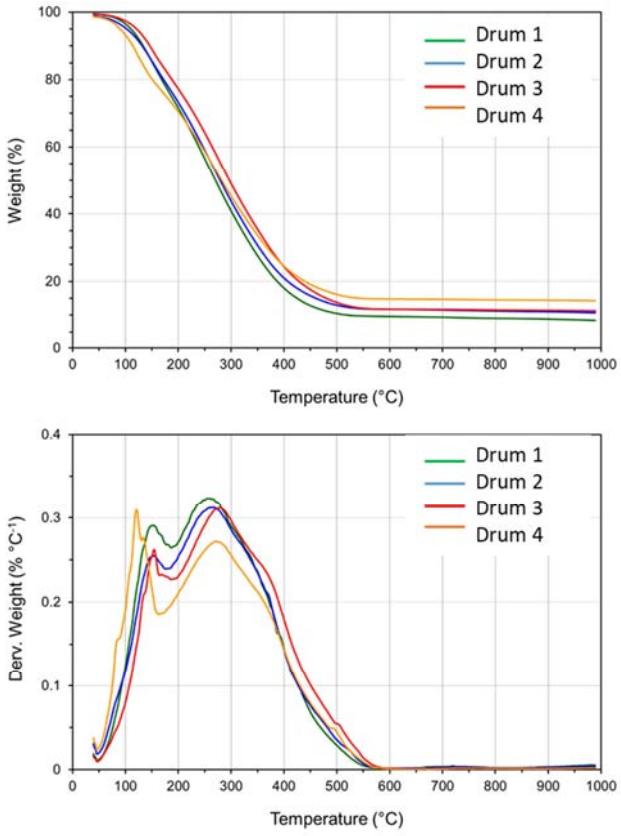

Figure 6. *TGA graph obtained for coal tar pitch samples.*

7. FTIR Analysis of Coal Tar Pitches

The coal tar pitch exhibits different molecules and surface functionality. It leads to diverse surface composition of coal tar pitch. Fourier transform infrared spectroscopy (FTIR) was carried out to analyze the surface functionality present in different coal tar pitch samples [8]. The FTIR spectra of different coal tar pitch samples have been compared in Figure 7. As seen in the figure, all the samples have almost same surface functionality. The peak observed at 3040 cm^{-1} confirms the presence of unsaturated aromatic bonds.

8. Applications of Oils (Volatiles)

The oils collected in receiving flask as a volatile through condenser are very useful for many applications. These oils are mixture of light oils (110-170°C), middle oils (170-230°C), heavy oils (230-280°C) and green oils (280-360°C). Light oils contain light oils such as toluene, benzene and xylene and can be used as solvents, dry-cleaning fuel, preparing dyes, drugs and other aromatic compounds. The naphthalene oil contains naphthalene and a range of tar acids and tar bases. Pure naphthalene is used to make dyes, drugs, explosives, mesophase pitch, carbon nanomaterial, phthalic anhydride, an intermediate for plasticizers, polyesters and resins, etc. Creosote oil is used for prevention of wood and disinfectants, etc. Anthracene oil mainly contains polynuclear hydrocarbons, such as Anthracene, phenanthrene and pyrene and are used for alizarin dyes and shows green fluorescence and they may be a good source of carbon black oil. To maximize the value from the byproduct of coaltar distillation process, the air-blowing technique is very useful anthracene oil at temperatures over 250°C are produces polymerization and condensation reactions between the main anthracene oil components, giving rise to air-blown products with possible industrial applications as precursors of graphitizable carbons. [14]

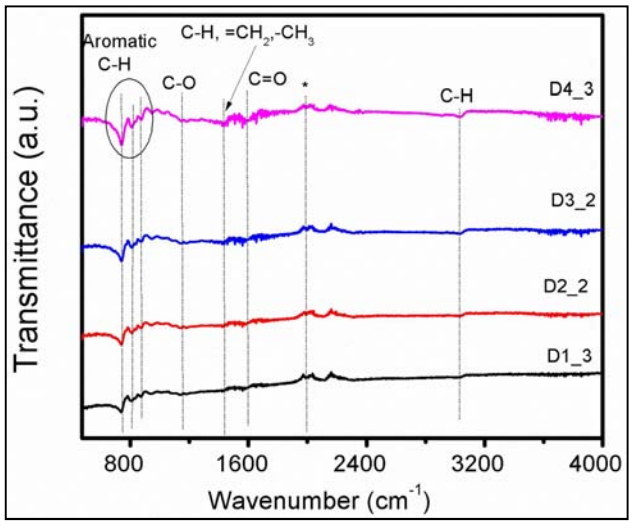

Figure 7. *FTIR of coal tar pitches.*

9. Conclusions

The major conclusions are as follows:

Four different coal tar samples have been characterized for various properties such as insolubility in quinoline and toluene, carbon content (coking value), ash content, viscosity, flash point, pour point, etc. It is seen that drum 1 has higher QI content and drum 4 has minimum QI content.

Three types of binder grade CTP and one impregnating grade CTP have been prepared using coal tar of drum 1, suitable for making binder grade coal tar pitch for aluminum industry & Graphite industry. But, it can also be used for development of binder grade coal tar pitch required for graphite industry by increasing the soaking time during distillation. QI free impregnating grade coal tar pitch having softening point of 88°C and QI content of 0.53% has also been obtained by reducing the QI of coal tar pitch sample by sedimentation process using suitable solvents.

From various experiments, it can be concluded that coal tar of drum 2 is suitable for making binder pitch for both aluminum and graphite industry as its QI can be easily tailored by changing the temperature and soaking time. On conversion of coal tar sample into coal tar pitches, QI content depends on distillation temperature, vacuum and soaking time. If softening point of pitch is <100°C then it can be converted into impregnating grade coal tar pitch by reducing the QI using sedimentation process.

Coal tar of drum 4 is the best suited material for making impregnating grade CTP.

Figure 8. *Coal Tar Pitch Samples.*

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