Speciality Cokes from Coal Tars:

A combined solution for graphite electrodes and Al cathodes

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Abstract

There is a growing demand from the steel industry for super premium needle cokes requested for the UHP arc furnaces producing electrical steel. The strong increase of the Al consumption and the switch to graphitized cathodes in the Al smelters raise dramatically the consumption of hard isotropic coke for this application. China and India where the growth rate in steel and Al exceed two digits face a challenging situation for the supply of high quality cokes for both carbon electrode applications. For instance the majority of premium needle coke is still imported in both countries and there is no production of needle cokes in India.

The lack of significant production of the above mentioned type of cokes in the petroleum refineries is related to the scarcity of low S decant oil generated by FCC units and to the lack of high asphaltene resids that are the preferred delayed coker feedstock for the production of relatively isotropic hard coke used for graphitized cathode.

The pig iron production is reaching in 2012 more than 700 mt in China and 40 mt in India. In China more than 500 mt and in India about 30 mt of coal was needed for covering the metallurgical coke consumed by the blast furnaces. With an average 3.3 % coal tar by product rate, the amount of coal tar exceeded 15 mt in China and reached 1 mt in India. The percentage of coal tar distilled for the production of pitches used in the domestic carbon industry reached only 20 % in China and 40 % in India. A significant proportion of coal tar binders are exported especially from India, however with mitigate economics.

The economics of tar distillers producing coal tar pitch can be massively improved when specialty cokes instead of binders are produced. Therefore the production of soft and hard cokes out of coal tar for, respectively, the graphite electrode and cathode applications represents an opportunity for the tar distillation but also for the users in the carbon industries.

The technical and economical aspects of the production of specialty pitch cokes are addressed along with forecast of the demand resulting from a market study. Innovative process for a balanced production of both type of cokes are discussed along with the impacts on the end-products performances that were tested at the electrode pilot scale and research laboratories.

Introduction

While no pitch coke is produced in India the situation has started to change in China some years ago so far specialty cokes are concerned. Apart the two decades old Baochem plant in Shanghai , producing mainly conventional pitch coke for the recarburizer application, needle cokes mainly for regular power EAF electrodes are yet produced by Sinosteel and Hongte. Some other projects were announced recently. However the quantities of premium needle cokes used for UHP electrode remains small and such high quality materials are still imported.

Significant amounts of large size UHP graphite electrodes and graphitized cathodes are consumed for which most of the specialty coke raw materials are not available in the country. Consequently there is a need for developing these specific raw materials, namely needle coke and cathode cokes, to respond to the domestic demand but also to the potential of export volumes of both finished carbon products.

Concerning the liquid feedstocks, slurry oils from FCC refinery units and derivates of tars from the cokeries carbonizing coals, can be considered for the production of premium needle cokes and the corresponding electrodes UHP electrical arc furnaces. For cathode cokes, low S with high asphaltene resid from vacuum crude oil distillation units, as well as some coal tar pitches is known to give after delayed coking and calcining the preferred cokes for abrasion resistant cathodes.

The situation and evolution of the

- petroleum refining industry,
- tar distillers and coke calciners,
- electrode and cathode manufacturers,
- crude and electrical steel industry and of the
- aluminium industry

in India and in China, that have a massive impact worldwide, shall be considered to assess the opportunities of producing speciality cokes at the horizon of 2020.

Concerning the availability of tars the table 7 in the appendix gives an overview of the figures taken for the estimation of the tars consumed for the carbon industry, which is a portion ranging between 20 and 40 % of the tars produced as a by–product of cokeries. Therefore, despite the competition from fuel applications, coal tar availability is and will be sufficient for the speciality coke production.

In this paper a solution for a combined production of needle and cathode cokes out of coal tar is presented.

Status-quo and outlook of the metal and carbon industries

Aluminium industry

For each ton of new Al-smelting capacity about 30 kg of new cathodes are needed and replaced 6 to 9 years later. About 6 kg of replacement cathode blocks per ton of metal are needed. Graphitized cathodes gradually replace amorphous anthracitic cathode blocks as it offers substantial metal capacity increase through cell amperage increase. Worldwide today about 30 % of cathodes are graphitized grade blocks but 50 % of new smelter pots are equipped with graphitized cathodes. This trend will lead to an increase to 35 % graphitized replacement blocks and to 60 % for the new installed capacity Al in 2020.

The capita consumption in India is at a very low level just above 1 kg Al/y and the domestic smelters cover this need with their 2 mt capacity. A small part is still exported but the domestic growth rate is close to 10 %. By 2020 a level of 4 to 5 mt Al production has to be expected.

Worldwide the growth is dominated by the impact of China where the annual production will double by 2020 and the capita consumption (25 kg/y) will reach practically a western world level. Beyond 2020 the future of Al in India is even brighter as potentially the capita consumption will increase by a factor 5 to10 for reaching western world standards.

The anode sector is by far the main indirect consumer of coal tar. The gross consumption of prebaked anodes is about 0.6 t per t of metal. As the coal tar pitch content is 15 % in the green anodes the needed coal tar amounts to 0.18 t per t of metal.

Steel Industry

In electric arc furnace, producing steel out of scraps, 2.5 kg of graphite electrode is used per ton of metal. The consumption of graphite electrodes has continuously dropped over the last decades as a result of better operation and technology advances in the arc furnace as shown in the figure 1. This explains why the total graphite electrode demand has been relatively flat, but the asymptotic current level of the specific consumption means that with any increase of the electrical steel production the electrode demand is today growing. Green graphite electrodes contain about 20 % of coal tar pitch so that about 0.4 t of coal tar per ton of graphite electrode is indirectly directed towards this application.

The steel industry plays then a dual role concerning the carbon materials. Tar is generated as a by-product of the metallurgical coke prepared by coal carbonization and used for the pig iron production in blast furnaces. For 1 mt of iron about 0.5 mt of coke is used so that from the 0.7 mt of coal needed 2200 t of coal tar are produced by the cokery.

In India the apparent capita consumption of finished steel is about 60 kg while it reaches 450kg in China where 700 mtpy of crude steel are produced today. In 2012 the Indian crude steel producers reach a level that is 10 times lower but for 2020 the target is above twice the current figure. The percentage of electrical steel reaches 30 % in countries that were booming in the mid of the last century, while it lies below 10 % in China that will enjoy a major development in this sector in the year to come.

Chinese government target is 20% by 2020, which would mean around 200 mtpy of electrical steel and 500’000 t of graphite electrodes, a level that will be difficult to reach. The yearly figure for India will move from the already high current 30 mt electrical steel towards 60 mt with a domestic use of 150’000 tpy of graphite electrodes.

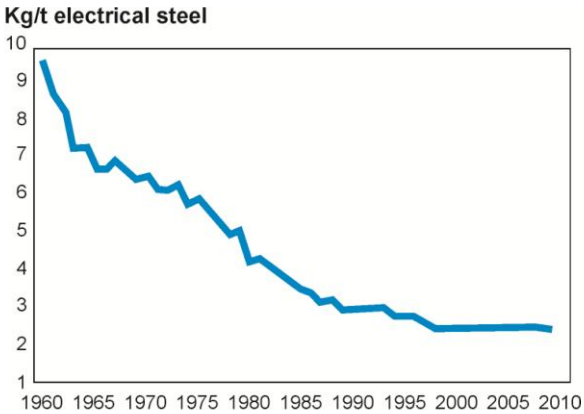

Figure 1: Specific Graphite Electrode Consumption

Electrode manufacturers

The current capacity of the Indian producers reaches already 150’000 tpy, so that a good part of electrodes are today exported, but in 2020 an increase of capacity by 50% has to be anticipated for maintaining the exports levels. The situation is even more extreme in China, where the capacity is five times higher, but the domestic use just twice the one of India. Both countries feel the progressive switch from RP to HP and ultimately to large diameter UHP electrodes for which regular cokes cannot be used.

The race to get super premium needle coke has started some years ago with substantial price increase as a consequence. Imports from Europe, USA and Japan, where the major needle coke producers are located, are today the sole but costly solution for India and China.

Graphitized cathodes are not manufactured to a significant production level in India. In the countries mentioned above, the graphite electrode plants were also producing cathodes in the past because they could easily recycle graphite scraps that were used with anthracite in the amorphous blocks. This is still the case today because graphitized cathodes represent an interesting swing capacity.

With the growing Al industry in India, this advantage and potential will be surely considered by the major electrode players. By 2020 about 15’000 tpy of graphitized cathodes will be used in India but the expansion of the smelting capacity beyond this date will bring this number to the current level of the graphite electrode capacity. In China the development of high amperage Al cells requests already today about 45’000 tpy of graphitized cathodes. This number will rise to 130’000 tpy in 2020 so that large quantities of erosion resistant coke raw material will be badly needed.

Coke calciners, petroleum and tar industries

The leading merchant calciners are active in the Al grade production, but not in speciality cokes that are calcined by the companies producing the speciality green cokes. The majority of the 1.2 mt needle cokes is produced by delayed coking of decant oil, a by–product (slurry oil) of the FCC units in high conversion petroleum refineries. In India the scarcity of such feedstock, that should be also low in Sulfur, explains the quasi absence of needle coke producers.

The delayed coking techniques used for needle cokes were developed four decades ago when the needle coke demand was growing rapidly [1]. Low S thermal and ethylene tars have been used in the production of needle cokes [2,3] but modern refineries and petrochemical plants have minimized these by-products to very low levels. The stagnation of the volume of this type of low S feedstocks in USA and Europe means that the increase of needle coke production there is very limited.

In Japan more than 100’000 tpy of pitch needle cokes are produced in two companies, using treated soft coal tar pitch as feedstock of delayed cokers since decades, but the availability of tars is the limiting issue of expansion.

The Chinese industry has started a development program having the goals to be independent of needle coke imports but the technical difficulties for producing super premium needle cokes are still not fully overcome. Efficient extraction of the lighter components present in the soft pitch (a step wrongly referred as QI removal), formation of needle coke structure during coking and high temperature calcining are the major hurdles for producing the super premium cokes needed for UHP electrodes.

For the cathode cokes one feedstock option would be desulfurized high asphaltene resid that is resulting in relatively isotropic hard shot cokes. Here again the lack of such feedstock in China and India, related to the crudes processed but also to the configuration of refineries, means that no development is to be expected on this route. This kind of low S shot coke is also a rarity on a worldwide basis so that a limited expansion of its production is an issue for the cathode producers.

In Japan and in South Africa cathode cokes out of coal tars have been developed in the last decades. The delayed coking of high QI and heteroatom rich soft pitch is a route that is proven to provide a hard coke that is resistant to the wear occurring in the Al pots. However the quantities of tar available limit the output to the current level of production as well.

The table 1 below summarizes the quantities of cokes needed for the graphite electrode and graphitized cathodes in India, China and worldwide. The quantities of cathode cokes covering the needs of graphitized cathodes by the domestic smelters will triplicate in India and in China by 2020. Whereas the today's quantities are not economically attractive to a newcomer on the calcined coke scene the situation will change and on a worldwide basis 250'000 tpy of such cathode coke will be used. This has to be compared to a typical speciality coke calciner who is dedicating today about 25'000 tpy for this application, practically the quantity that will be consumed internally in India by 2020 through graphitized cathodes.

For needle cokes, the 2020 consumption for electrical steel in India will reach 170'000 tpy which is about the typical size of one leading calcining plant today. In China more than 500'000 tpy of needle coke will be needed. As plenty of tars will be theoretically available in India (more than half of the 1.9 mtpy produced from the pig iron industry) and in China (2/3 of 18 mtpy) the choice of tar distillers could be to expand the current production resulting in coal tar pitch binders also for exports or/and to embark into the production of speciality cokes when the economics are more favourable for these end-products. On the long term this route of pitch coke based on tar is sustainable on a worldwide basis as long as the pig iron steel production exceeds 9 times the Al figure. The today ratio is about 25 and this number was quite stable over the last decades.

		India		China		World	
		2012	2020	2012	2020	2012	2020
Cathodes							
Al Production	mt	2.0	4.2	15.0	32.0	42.0	69.0
Replacement cath.	10^4t	1.0	2.5	9.1	19.2	25.2	41.4
New smelters cath.	10^4t	0.6	1.3	4.5	9.6	8.8	14.5
Graphitized cathodes	10^4t	0.6	1.6	4.5	13.0	10.0	23.0
Electrodes							
Graphite Electrodes	10^4t	8	15	19	45	113	163
Cokes (domestic use for metal production)							
Cathode Coke	10^4t	0.7	2	5	14	11	25
Needle Coke	10^4t	9	17	21	50	124	180

Table 1: Cathode, Electrode and coke requirements

Production of pitch cokes by delayed coking

Coking of straight soft pitch

Pitch coke production by delayed coking of soft pitch from the primary tar distillation was initiated in the sixties by Nittetsu Chemical Ind. in Japan using American technologies adapted from the petroleum industry [4].

The pitch coke was used in the Al industry and as recarburizer. Later in the eighties, a unit processing medium temperature pitch issued from the coal gasification process was installed in South Africa. By blending with decant oil a hybrid coke fulfilling the expectations of the Al smelters could be reached, but the pure pitch coke could not be used as thermal cracking of prebaked anodes was an issue. In the last decade however the pure material was successfully used for the graphitized cathodes as its hardness provides a good resistance to the wear and erosion of the blocks.

However despite their low S content such straight pitch cokes could not be used for the graphite electrode application because of their non-needle structure.This is related on one side to the presence of large aromatic molecules hindering the coalescence of mesophases during the coking or to the presence of non-planar molecules that are poorly graphitizable[5]. The fine-grain mosaic structure of the resulting coke, that is quite hard[6], gives an isotropic electrode with high CTE and resistivity. Another issue is the presence of Nitrogen in the coal tar[7] as the loss of these heteroatoms during the graphitization process[8] results in an irreversible large expansion of the graphite electrode with cracks and scrap issues in modern Length Wise Graphitization (LWG) furnaces. The extent of puffing is however much more reduced when the coke structure is isotropic[9] so that puffing of cathode blocks during graphitization was found to be far less problematic.

Coal tar feedstock treatment

The treatment of the coal tar or of the coal tar pitch feedstock is mandatory for the production of premium needle cokes and this received already in the eighties much attention [10] so that several options for the removal of large molecules (a fraction Insoluble in Quinoline named QI) by filtration, centrifugation and sedimentation have been considered.

However the route consisting in the extraction of lighter molecules was found to be the most promising one already by Nittetsu in the seventies[11]. Many patents have been applied on this topic and often the solvents are a blend of aromatic distilled tar oils (for instance Naphtalene with an aliphatic petroleum fraction like Kerosene[12]). The amount of the extracted fraction, and therefore also the potential of the extracted feedstock to provide later the needle coke structure, depends on the nature of the tar oil fraction chosen [13], that can range from benzene to anthracene, and on the aromatic/aliphatic ratio of the blend solvent.[14] More recently options involving acetone like solvents combined with screw decanting has been patented [15] and the selection of solvents and extraction steps favourable to the removal of N rich components have been considered[16].

The use of similar techniques by the coal tar distillers to manufacture impregnation pitches for graphite electrodes shows that these techniques are familiar in this industry. However the selection of the solvents, the separation of the fractions and the recovery process are decisively influencing the quality and the quantity of the coker feedstocks that are the so-called QI free and QI rich soft pitch fractions.

Obviously in the last decades the QI rich fraction was sold as a binder for non-sophisticated application and not directed to the coker due to its small volume and to the lack of high value application of the produced isotropic hard coke. Due to the recent new application as graphitized cathode coke and the growth of the Al industry the situation might change especially when more similar feedstocks resulting in hard carbon would be available. One opportunity is to benefit from the developments made in the last decade on the polymerization of heavy tar fractions like anthracene for producing pitch but to extend them to the coke production by delayed coking.

Polymerizering of heavy oils

Air-blowing for the production of asphalt from petroleum resids or even for the production of coal tar pitch binders is a well-known and applied technique. The relative low market value of anthracene oil in the late nineties has pushed some tar distillers and research institutes to consider the production of carbon precursors[17] out of polymerized anthracene. Sophisticated industrial applications like mesophase based carbon materials have been targeted[18] with mitigate success as the yields were also low while the production of binder pitch was industrially experimented[19].

Some developments for environmentally friendly pitches using this route are still made[20] but we do consider that the economics would be much more favourable for coking these pitches in view of the production of speciality cathode grade coke.

The effect of air injection is not only to accelerate the polymerization of the pitch by condensation reactions but also to introduce oxygen containing molecules into the pitch.

The strong cross-linking effect of these molecules [21] result in a mosaic structure of the coke, which is precisely the preferred carbon for graphitized cathodes. Of course the heavy coker oil fraction can also be directed to such a simple polymerizer to extend significantly the amount of isotropic coke produced in the delayed coker. For the lighter oil fractions of the coker and of the primary distillation of tars, the air–blowing is not efficient so that a catalytic process is needed, but here the target pitch is a feedstock for the production of needle coke.

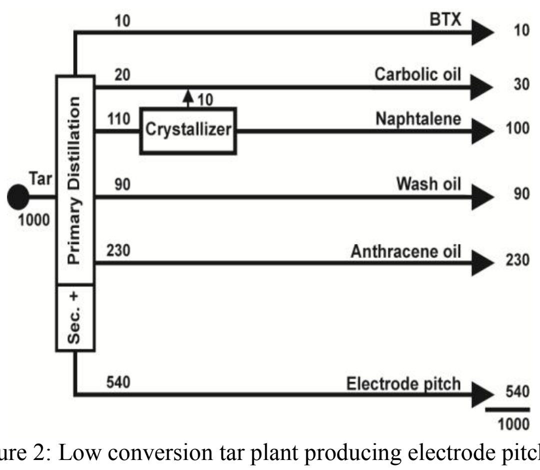

Figure 2: Low conversion tar plant producing electrode pitch

Catalytic carbonization of light oils

Lewis acids like $FeCl_3$ and $AlCl_3$ have been recognized to be excellent catalyst to provide anisotropic needle like carbons from light aromatic hydrocarbons as naphthalene and this at a high yield[22]. Synthesis of mesophase pitch using strong Friedel-Craft catalysts for aromatic condensation has been developed as well. A mixture of HF/BF_3 for instance allows a complete catalyst removal from the pitch product with a full recovery and easy recycling thanks the low boiling points of both components[23].

Producing specialty cokes from coal tar

Production scheme from low to ultimate conversion

The current tar distillers mainly produce electrode pitches with medium to high softening points while emphasis is given in the production of high purity naphthalene. In this low conversion scheme (Figure 1) from tar to carbon, high amounts of anthracene oils are produced and sold as carbon black feedstock at a low price close to the one of the incoming tar. A typical new distillation unit has a tar capacity of 300'000 tpy consists in a primary distillation unit delivering a low softening pitch under atmospheric pressure and a secondary unit, working under vacuum, where at high temperature heavy aromatics are removed and the final electrode pitch is obtained.

This secondary process step is not needed when delayed coking is considered as the feedstock is a low softening point pitch produced directly with the primary distillation unit. In the gradual up-grade of a tar distillation plant producing cokes rather than pitch, as shown in the Figure 3 to 5, more and more sophisticated coker feedstocks are produced for maximizing high value coke productions and minimizing low price heavy oil outputs. BTX and high value pure naphthalene are maintained as liquid outputs as pitch coker feedstock preparation through severe catalytic process were found to be inefficient for these light aromatics.

Medium conversion tar plant

With this scheme (Figure 3) coal tar pitch binder is no longer produced. The soft pitch is passed into a simple solvent extractor where the heavy fraction containing the QI molecules is separated by gravity settling. The primary goal is the production of needle cokes but the production of cathode cokes can be considered as well as this basic extraction unit delivers a significant amount (up to 1/3) of heavy pitch fraction.

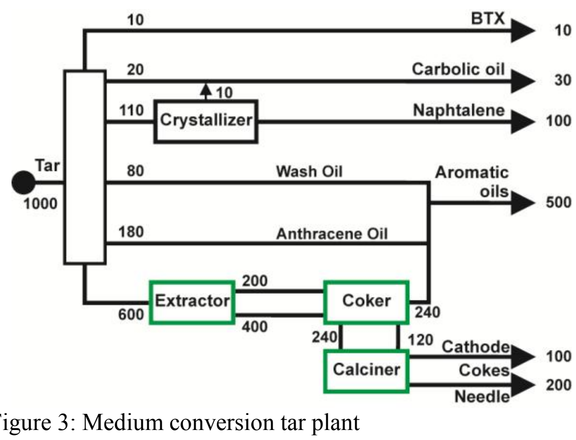

Figure 3: Medium conversion tar plant

The delayed coking, made campaign wise, results in about 60 % coke yield and 40 % liquids that are blended with low value oils from the primary distillation unit. After calcining in a high temperature rotary kiln at a coke yield of 80% about 20 % of calcined needle coke and 10 % of calcined cathode coke are obtained from the incoming tar.

This scheme can be considered as standard and state of the art in the industry so that buying a technology package can be anticipated.

High Conversion tar plant

In this scheme the quantity of needle coke is increased by better separation efficiency in the extraction step through additional centrifugation (Figure 4). The quantity of aromatic oils is practically halved by passing the heavy coker oils and the primary distillation anthracene in the polymerizer that will provide a substantial increase of the amount of cathode coke after campaign-wise delayed coking and calcining.

For the polymerizer unit a licensing agreement with companies having already industrial experiences shall be negotiated. Centrifugal separator of liquids for the up-grade of the solvent extractor are well spread in the chemical industry, but semi-industrial trials should be run to fine tune this technique to the specificity of the solvent and tar components to be treated. The hurdles towards an industrial unit integrating both up-grades can be overcome in a relatively short time at reasonable development costs.

Ultimate Conversion tar plant

The ultimate goal is eliminating the low value aromatic oils from the tar plant thanks a catalytic carbonization unit processing the light coker oils and the primary distillation wash oil (Figure 5). This will raise the quantity of finished needle coke close to 40% of the tar input and suppress the output of low value aromatic blend oils. The catalytic carbonization process was developed for mesophase pitch and is still at the pilot scale; the design adaptations and the selection of process parameters shall be addressed first at this pilot scale and an industrial unit developed with an engineering company having in mind that the quality of the needle coke produced should meet the specifications of the graphite industry. With this scheme, more than two thirds of calcined coke can be potentially produced but the economics shall be considered to quantify the incentive to develop and use this costly ultimate step.

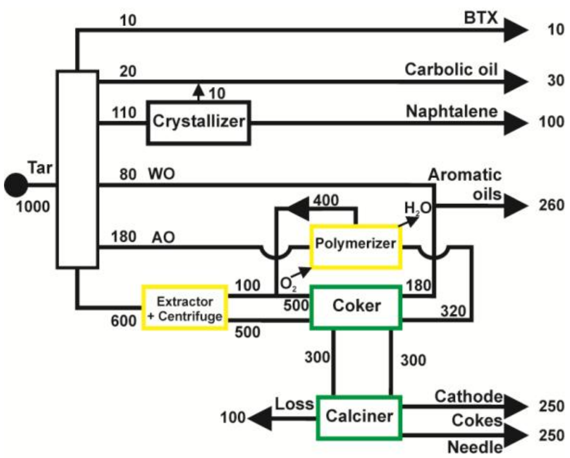

Figure 4: High conversion tar plant

Investment and operating costs, turnover and margins

The total investment costs for the three conversion levels are compared to the one of electrode binder production in the Table 2 for a name plate tar distillation plant of 300'000tpy capacity to be built in the western world using modern technologies. The investment costs taken here are the worst case figures to be considered and building such unit in China or India can cut costs by more than a factor two.

The same remarks apply for the operating costs in Table 3 as personal wages are remarkably lower than in the western world. For the turnover shown in Table 4, western figures have been taken as well, but the local domestic market can be different especially for the coke prices. The margin estimated here in Table 5 are therefore valid for the western world and adaptations to the Indian or Chinese situation remained to be made, but the trends observed for the different conversion levels are a first basis to assess the potential and attractiveness of the production of cokes from tar.

The investments costs of 100 m$ for a 300'000 tpy tar distillation plant producing electrode pitch double, triplicate and quadruplicate for respectively the medium, high and ultimate conversion levels. The operating costs follow more or less the same trend. The yearly turnovers are more or less always around the investment costs. This means that, without detailed calculation of the rate of return, the economics look promising. The margin increases from a low level of 60 $/t of tar processed for the basic low conversion scheme producing binders to 640 $/t for the ultimate conversion level producing a maximum of coke products. For a progressive up-grade approach, prior all the developments in polymerizing and catalytic carbonizing have been performed it is good news to see that the increase of the margin is substantial for the proven medium conversion scheme as it already reaches four times the low conversion one.

The requisites for coke production out of tar

Industrial background

The fundamentals for coke production are surely gathered in China and in India. The electric steel production is well established and steel scrap availability increases steadily. The Al industry has a huge growth potential and mega projects using modern technologies with graphitized cathode lining have been realized recently and more are to come for covering the domestic needs.

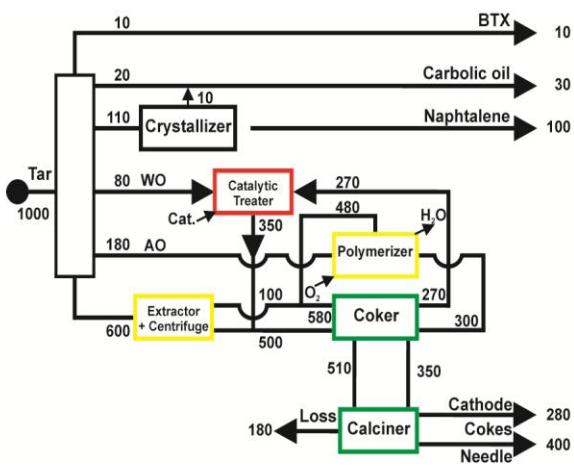

Figure 5: Ultimate conversion tar plant

Process	Low		Medium		High		Ultimate	
	Ktpy	MM$	Ktpy	MM$	Ktpy	MM$	Ktpy	MM$
Tar distillation	300	95	300	95	300	95	300	95
Crystallizer	33	5	33	5	33	5	33	5
Soft pitch preparation	-	-	180	10	180	15	180	15
Coker	-	-	180	40	300	65	430	80
Polymerizer	-	-	-	-	120	35	140	40
Catalytic Treater							105	75
Calciner (calcined coke)	-	-	90	60	150	85	205	110
Total		100		210		300		420
Sp. Investment $/t tar		333		700		1000		1400

Table 2: Capacity and investments for 300’000 tpy tar plants

Process	Low		Medium		High		Ultimate	
	$/t_{feed}$	$/t_{tar}$	$/t_{feed}$	$/t_{tar}$	$/t_{feed}$	$/t_{tar}$	$/t_{feed}$	$/t_{tar}$
Tar distillation	43	43	43	43	43	43	43	43
Crystallizer	20	7	20	7	20	7	20	7
Soft pitch preparation	-	-	25	15	35	20	35	20
Coker	-	-	70	45	50	50	40	56
Polymerizer	-	-	-	-	70	30	60	24
Catalytic Treater							85	30
Calciner	-	-	65	20	40	20	30	20
Total $/t_{tar}$		50		130		170		200

Table 3: Operating costs for 300’000 tpy tar plants

The Indian and Chinese electrode producers have a long and good reputation and benefits of the low cost of their operations, but the high costs of imported needle coke remains a burden. Their experience in the graphitization and machining will be an asset for expanding their carbon plants towards graphitized cathode products.

The crude steel production is steadily growing for covering the domestic consumption so that more tar will be available for coke production by delayed coking and calcining. Thanks the production of impregnation pitches (low QI content), which is performed at a large scale in both countries, the preparation of the soft pitch prior coking is a familiar process. However the external input of leading technology providers in these areas is recommended to boost rapidly the progress towards technologies fully adapted to the needle coke and cathode coke productions.

A turn-key solution without basic and applied research and development is unfortunately not available. There are plenty of experiments, from the laboratory to the semi-industrial scale, to be executed prior an industrial project can be considered. R&D Carbon is fully equipped for responding to these requirements.

R&D Carbon pilot testing facility

In the fine tuning of the soft pitch preparation, precise answers on the coke performance during the manufacture and usage of the carbon end-products shall be given. Bomb coking in small pressurized vessels and microscopic examination of the coke structure can be used as a first screening tool but a chain of pilot units i.e. coker, calciner and carbon pilot plants are mandatory for minimizing the risks and accustoming the end users to the new type of raw materials and end-products.

The pilot coker shall be continuous with coker oils fractionation for mass balances purpose[24]. Recycling ratio, temperature and pressure shall be easily controlled and the coker drum size shall deliver about 100 kg of green coke for which the sizing, VCM and HGI level should be optimized for the graphite or for the cathode application.

Products	Price	Low		Medium		High		Ultimate	
	$/t	‰	Value	‰	Value	‰	Value	‰	Value
BTX	460	10	5	10	5	10	5	10	5
Carbolic oil	290	30	9	30	9	30	9	30	9
Naphtalene	880	100	88	100	88	100	88	100	88
Wash /aromatic	340	90	31	500	170	260	88		
Anthracene oil	280	230	64						
Electrode pitch	400	540	213						
Cathode coke	900	-		100	90	250	225	280	252
Needle coke	2300	-		200	460	250	575	400	920
Total		1000	410	940	820	900	1000	820	1270

Table 4: Specific turnover for 1t of tar

Investment $/tpy tar		Low 333	Medium 700	High 1000	Ultimate 1400
Capital* cost	$/t tar	40	90	120	170
Operating cost	$/t tar	50	130	170	200
Tar cost	$/t tar	260	260	260	260
Total Prod. Cost	$/t tar	350	480	550	630
Turnover	$/t tar	410	820	1000	1270
Margin	$/t tar	60	340	450	640

** 10 year SL + 20% for Working capital*

Table 5: Specific production costs, turn over and margin

Calcining in a pilot rotary kiln, where the heat-up rate is set close to these of industrial units is essential as the calcining influences the porosity level of the calcined cokes. Such a unit having a throughput of 20 kg/h is shown in Figure 6. The heat-up rate in the devolatilization zone reaches 50 C/min.; the residence time is close to 20 minutes. The final temperature treatment is selected to get a typical level of real density (2.14 kg/dm^3 for needle coke and 2.02 for cathode coke).

The preparation of dry aggregate and especially of the fines is essential for a sound evaluation of the performance of the cokes. The puffing behaviour related to the rapid heat-up during graphitization depends on the grain size[25], especially for pitch needle coke electrodes, the lower the fineness of the fines the higher the puffing rate and extent. The CTE of the graphitized electrodes also depends on the maximum grain size , coarser formulation meaning higher CTE, so that lab scale preparation and testing of pure fines artefacts can lead to wrong information on the quality of a given coke candidate[26].

For these reasons the maximum size of grains shall be larger than 6mm and the amount and fineness of fines in the recipe shall be close to industrial standards. Such dry aggregate preparation tools are shown in the Figure 7. As the properties of the end-products depend on the pitch content, several batches are prepared and will be used with at least three different pitch levels (around 23 % of the coke aggregate).Intensive mixing and high pressure extruding are needed as well to get artefacts with similar apparent density and mechanical/electrical properties levels than full size not-impregnated electrodes or cathodes. Intensive mixer impeller (Figure 8) together with large diameter (above 70 mm) pilot extruder was found to be adequate for the pilot evaluation purpose (Figure 9).

The baking is made with moderate heat –up rate for minimizing deformation related to the high percentage of electrode binder and graphitizing is made under pressure like in a Length Wise Graphitization pilot furnace (Figure 10). For this purpose 50 mm baked cores are stacked into a 500mm column, eventually pressed with a 7.5 MPa specific pressure that guarantees a good electrical contact.

Figure 6: Rotary kiln (L=6m ø25cm) for coke calcinations

Figure 7: Pilot plant dry aggregate preparation

Figure 8: Intensive impeller mixer for high density paste (10 l)

A DC current is applied for heating the baked specimen up to 3000 C with a controlled temperature gradient of 500 C/h. With these conditions close to the full size modern LWG the dilatation (thermal and puffing) and the contraction related to the graphitization are monitored.

Of particular interest for needle cokes is the dilatometric curve of transversal electrode cores where the puffing propensity can be best observed (see Figure 11). The lab extrusion of small diameter (19 mm) artefacts made out of fines and high binder content (up to 38 %!) was found to be inappropriate for this purpose as transversal core dimensions become very small.

Figure 9: 400 tons extrusion press for 85mm green rods

Figure 10: 80 kW LWG graphitizing furnace

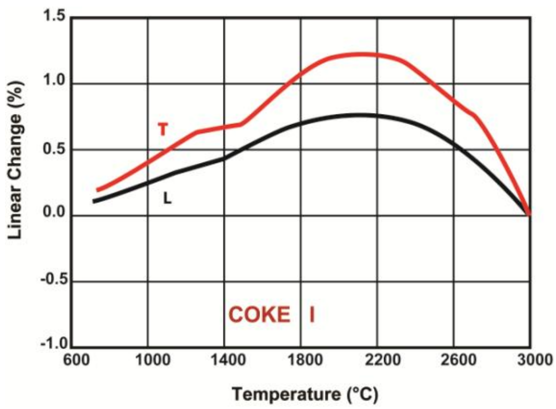

Figure 11: Longitudinal / Transversal cores (L/T): dilatometric curves during graphitization

A graphitization under pressure become impracticable and puffing measurements anyhow biased as mentioned previously.

A research laboratory where specific electrode properties can be measured, like for instance the swelling of cathodes during electrolysis and its abrasion resistance, completes the testing facility.

Evaluations of worldwide cokes for graphite electrode and cathode have been performed so that typical ranges as shown in the Table 6 have been established.

Coke Properties	Unit		Typical range Pitch needle cokes			Typical range Cathode cokes	
Sulfur	%		0.2 - 0.3			0.2 - 1.0	
Nitrogen	%		0.5 - 0.7			0.7 - 1.5	
Total Porosity <100µm	%		19 - 22			12 - 16	
Density in Xylene	kg/dm^3		2.13 - 2.15			1.98 - 2.05	
Green and baked							
Pitch content	%		24 - 26			16 - 20	
Green App. Density	kg/dm^3		1.57 - 1.66			1.60 - 1.70	
Baked App. Density	kg/dm^3		1.54 - 1.61			1.55 - 1.65	
Graphitization Behaviour			**L**	**T**		**L**	**T**
Puffing Rate	$10^{-6}K^{-1}$		5 - 8	5 - 18		1 - 6	2 - 12
Puffing extent	%		0.25 - 0.35	0.15 - 0.70		0.1 - 0.3	0.1 - 0.5
Cold diameter change	%		0.4 - 2.5	-		(-1) - (+1)	-
Cold volumetric change	%		(-1) - 4	-		(-4) - (-1)	-
Graphitized cores							
Graphitized App. Density	kg/dm^3		1.50 - 1.58			1.61 - 1.68	
Sp. Electrical Resistance	µΩm	**L**	9 - 11		**T**	10 - 14	
Flexural Strength	MPa	**L**	4 - 6		**L**	8 - 12	
CTE 20-300°C	$10^{-6}k^{-1}$	**L**	1.0 - 1.2		**L**	4 - 6	
Rapoport swelling	%		-		**L**	0.3 - 0.5	
Abrasion	%		-		**T**	14 - 28	

Table 6: Typical ranges of pitch needle cokes and cathode cokes and of their pilot artefacts

Merit ranking of coke candidates can be therefore made based on solid information on the electrode properties obtained with the current cokes used by the carbon industry. This pilot scale tool can be also used to quantify the benefits in terms of puffing when nitrogen removal techniques are applied to the aromatic coal tar oil feedstocks [27] or when puffing inhibitors are added to the calcined coke itself prior mixing [28], alternatively during the paste preparation[29].

Conclusions

The big potential of production and usage of pitch cokes in India for graphite electrodes and graphitized cathodes has been demonstrated. A progressive conversion approach is possible so that as a starting point a medium conversion plant producing a reasonable amount of pitch cokes for both applications can be contemplated at affordable investment costs. The quantity of cokes can be progressively increased for instance by adding one coker and one calciner unit when more oils are directed towards the pitch polymerizer and the catalytic carbonizer units.

However as the amount of tar needed is substantial and as the approval of end users is always a critical step, a partnership steel producer / electrode manufacturer / tar distiller would greatly facilitate such a project. Ideally the steel producer would supply tars from his cokeries and take from the electrode partners the finished graphite electrode for his electrical steel arc furnaces. The progressive introduction of high performance graphitized cathodes in the Al industry is also an issue that shall be well addressed by the electrode producers and leading Al smelting companies.

The advances can be speed-up when the right blend of foreign expertise and in-land engineering institutes is set-up from the very beginning of the projects. R &D Carbon can provide the services associated with the evaluation of the feedstock suitability for speciality cokes but also the technical expertise in the fields of feedstock preparation, delayed coking and calcining conceptual designs as well as the optimization support during the speciality coke plant start-up. Assistance to the end-users, for a smooth introduction of the speciality pitch cokes in their plants, can be given as well.

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Appendix

Appendix		India		China		World	
		2012	2020	2012	2020	2012	2020
Al Smelters							
Production	mt	2.0	4.2	15	32	42	69
Consumption	mt	1.5	3.4	16	34	42	69
Deficit / Excess	mt	+0.5	+0.8	-1	-2	0	0
Capita Cons.	kg	1.6	3.1	14	25	5.1	7.8
Steel							
Pig iron	mt	40	74	700	850	1130	1410
Elect. steel	mt	42	60	77	180	450	650
Elect. / crude steel	%	60	50	10	17	28	29
Carbon for domestic use							
Graphite Electrode	mt	0.08	0.15	0.19	0.45	1.13	1.63
Anodes (gross)	mt	1.2	2.5	9.0	19.2	25.2	41.4
Others							
Tar for Electrode	mt	0.03	0.06	0.08	0.12	0.45	0.65
Tar for Anodes	mt	0.36	0.75	2.70	5.76	7.56	12.42
Tar for other Carbons	mt	0.01	0.03	0.12	0.26	0.49	0.93
Total Tar for Carbon	mt	0.4	0.8	2.9	6.2	8.4	14.0
Tar from Coal	mt	1.0	1.9	14.4	18.7	24.9	31.2
Tar difference	mt	+0.6	+1.1	+11.5	+12.5	+15.5	+17.2

Table 7 : Availability of tars for pitch coke production