InfoMine research group

Association of Independent Consultants and Experts
in Field of Mineral Resources, Metallurgy and Chemical Industry

Petroleum Coke Market Research in the CIS

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Annotation

The report is devoted to investigation of current standing of petroleum coke market in Russia and other CIS countries and forecast of its development. The report is composed of 6 Sections, contains 168 pages, including 36 Figures, 83 Tables and 2 Appendices.

As information sources, we used data of Federal Service of State Statistics (Rosstat), Inter-State Committee on Statistics of CIS countries, Federal Customs Service of Russia, official domestic railage statistic of JSC RZhD (former Ministry of Railway Transport of Russia), Customs Services of other CIS countries, own InfoMine database, sectoral (industrial) and regional press, annual and quarterly reports of companies, as well as data from web-sites of company-producers and consumers of the products of interest.

In addition, some data were verified and corrected by the way of telephone interviews with specialists of companies, involved in petroleum coke market.

This all allowed experts of InfoMine to draw actual picture of petroleum coke market in the CIS and prospects of its development.

The first Section of the report presents data on resources, required for production of petroleum coke, and their characteristics. The Section also carefully describes technology of the coke production and quality parameters of the final products.

The second Section of the report presents analysis of petroleum coke (green and calcined) production in CIS countries, including statistical and estimated data on volumes of the coke production in Russia and other CIS countries. Besides, the Section presents detailed description of all company-producers of petroleum coke in Russia/CIS, their current standing and prospects of development.

The third Section of the report presents data on foreign trade operations in petroleum coke in CIS countries.

The fourth Section of the report presents data on producer's prices on various grades of coke at Russian market. Besides, it analyses data on dynamics of export-import prices on the products in Russia and Ukraine; in addition, forecast of the prices up to 2020 is given.

The fifth Section of the report analyses consumption of petroleum coke. The Section presents supply-demand balance of petroleum coke, sectoral structure of its consumption, presents the main consumers, as well as describes current standing and prospects of development of the greatest enterprise-consumers in Russia/CIS.

The sixth, final Section of the report presents forecast of development of petroleum coke market in Russia up to 2020.

The Appendices present contact information on producers and consumers of petroleum coke in the CIS.

Introduction

Petroleum coke (carbon of oil genesis, often abbreviated petcoke) is a carbonaceous solid derived from oil refinery coker units (delayed coking units) or other cracking processes. The product presents porous solid infusible and insoluble dark-gray to black mass. It is composed of high-condensed high-aromatic polycyclic hydrocarbons with small content of hydrogen, as well as other organic compounds.

Elementary composition of green (non-calcined) petroleum coke is as follows (%):

C: 91-99.5
H: 0.035-4
S: 0.5-8
(N+O): 1.3-3.8, and
the rest falls to metals.

Petroleum coke is complex disperse system, in which disperse phase is composed of crystalline elements of various size and order in mutual position of molecules and pores, and the disperse medium, filling pores in crystalline matter, is presented by continuous gaseous or liquid phase, forming adsorption-solvate layers, or solvate complexes.

Carbon is ordered to graphite structure fragments. Degree of ordering depends on raw material and technology of its preparation. For instance, directly distilled heavy oil residues yield low-ordered structure, whereas distilled cracking residues yield high-ordered one. Degree of ordering governs graphitization ability of petroleum cokes and properties of graphite obtained.

The main parameters of grade of petroleum coke are contents of sulfur, ash, moisture, yield of volatile components, granulometric composition (grain composition). The main properties of green cokes are given in Table 1.

Table 1: Properties of green coke

Parameter	low-sulfurous		sulfurous		high-sulfurous	
	> 25 mm	< 25 mm	> 25 mm	< 25 mm	> 25 mm	< 25 mm
Yield, mass %						
of fractions	41.5	58.5	35.7	64.3	45.0	55.0
volatile components	8.7	10.2	6.8	9.3	6.8	7.2
Content, mass %						
sulfur	0.52	0.53	1.2	1.37	4.0	4.07
ash	0.43	0.50	0.27	0.34	0.46	0.49
Mechanical strength, MPa	5.7	4.0	4.6	2.8	6.0	5.3
Porosity, %	16-56					
Bulk mass, kg/m^3	400-500					
Specific electric resistance, Ohm*m	$(80-100)*10^6$					

In content of sulfur, cokes are subdivided into low-sulfurous (below 1%), sulfurous (below 2 %) and high-sulfurous (above 2%). In content of ash, cokes are subdivided into low-ash (up to 0.5%), medium-ash (0.5-0.8%), high-ash (above 0.8%). In grain composition, cokes are subdivided into lumpy (fraction above 25 mm), "nut" (6-25 mm), fines (below 6 mm).

In method of obtaining, petroleum cokes can be divided into cokes, obtained by delayed coking, and by coking in heated stills.

Before use, petroleum coke is usually subjected to refining (calcinations) at oil refineries directly after obtaining, or by customers itself.

Petroleum coke is used mainly in metallurgy: for obtaining anode paste in aluminium production, graphitized electrodes for arc furnaces in steelmaking industry, for obtaining sulfidizing agents in nonferrous metallurgy (for conversion of metals or their oxides into sulfides to simplify the metals extraction from ores, for instance, in production of Cu, Ni and Co). Besides, in chemical industry petroleum coke is applied as reducer, for instance, in production of BaS_2 from barite, in obtaining CS_2, carbides of Ca and Si. Special sorts of coke are used as structural material in manufacture of corrosion-resistant apparatus. In food industry, coke is applied in sugar production as substitute of blast furnace coke.

1. Technology of petroleum coke production and resources used

1.1. Raw materials for obtaining petroleum coke

Grade of raw materials is a priority parameter, governing properties of final product – coke.

Production of coke in the CIS is mainly conducted at delayed coking units (DCU). A feature of DCU operation is the fact that the facilities use, as resources, various semis and wastes of oil refining at a refinery. As various oil refineries used different oils with different properties and yield, correspondingly, different semis and wastes, each DCU was designed for processing specific products to yield coke of required grade. As raw materials, heavy oil fractions, obtained by distillation (fuel oil, tar), cracking-residues of thermal cracking of fuel oil and tar, heavy gas-oil of catalytic cracking, oil production residues (asphalt, extracts of phenol cleaning oil, etc.).

The best petroleum residues for coke production are aromatic concentrates (distillate cracking residue) and some other high-molecular hydrocarbons.

Grade of coke is determined, first of all, by its sulfur content: sulfur is undesirable component of the product, decreasing its grade, and high-sulfurous and sulfurous cokes application is limited by power generation sector (as fuel). The thing is that sulfurous and high-sulfurous cokes encourage corrosion of equipment, increased quantity of fractures in electrode articles, breaking refractory lining of calcinations furnaces.

Petroleum, arriving oil refineries, varies in composition, especially in sulfur content. A feature of CIS and Russian oils is that they refer mainly to sulfurous and high-sulfurous type.

In the territory of the ex-USSR, a large share of Baku, Grozny, Sakhalin, Turkmen and a some Ukrainian and Kazakh petroleums refer to low-sulfurous (below 0.5%).

Sulfurous petroleum (0.5-2.5% S) is produced in Ural-Povolzh'e (Tuimazy, Romashinskoe oil fields, etc.), Western Siberia (Samotlor, Nizhnevartovsk, Megion oil fields, etc.).

High-sulfurous petroleums (above 2.5% S) is produced in Ural-Povolzh'e – Arlanskoe, Radaevskoe, Pokrovskoe oil fields.

Thus, the main raw material for coke production is now sulfurous petroleum.

According to Specifications (GOST 9965-76), petroleums are subdivided into 3 groups depending on degree of preparation, into 3 classes by sulfur content, and each class is subdivided into 3 types depending on density at $200^{o}C$) (Table 2).

Table 2: Specifications on petroleum for oil refineries (GOST 9965-76)

Depending on sulfur content				
Low-sulfurous	Up to 0.60%			
Sulfurous	from 0.61% to 1.80%			
High-sulfurous	above 1.80%			
Depending on density at 200°C, kg/m³				
Light	Up to 850			
Medium	from 851 to 885			
Heavy	above 885			
By parameters of preparation degree				
№ of Group	Chlorides concentration, mg/dm³	Moisture, %	Mechanical impurities, %	Saturation pressure, kPa
I	maximum 100	maximum 0.5	-	-
II	maximum 300	maximum 1.0	maximum 0.05	maximum 66.7
III	maximum 900	maximum 1.0	-	-

Source: FGUP Standardinform

Application of technologies, allowing to obtain high-grade coke independently of petroleum composition, solves many problems: provides electrode industry with grade resources, allows to use wider range of petroleums, and to deepen process of petroleum (oil) refining at oil refineries.

To de-sulfurize finished product, calcinations of coke is applied. One more way to obtain de-sulfurized coke from high sulfurous oils is preliminary cleaning oil of sulfur by hydro-desulfurization, hydro-cracking or de-asphaltization methods. This variant is considered to be more efficient, in spite of its complicity, and requires additional expenditures.

To the Russian refineries, oil is mainly supplied by the system of main pipelines of AK Transneft, in which West-Siberian oil of grade Siberian Light is mixed with more heavy and sulfurous oil of grade Urals.

In Table 3, the main suppliers of petroleum to oil refineries of CIS, producing coke, are presented.

Table 3: Suppliers of petroleum to oil refineries of CIS, producing coke

Oil refinery/Petroleum company	Lukoil	TNK	Rosneft	Bashneft	Tatneft	Gazpromneft*	Ukrnafta	KazMunaiGaz	MangistauMunaiGaz	CNPC-Aktobemunaigaz	Turkmenneft	Uzbekneftegaz	PetroKazakhstan	GNKAR
Novoil	+	+		+	+									
Ufaneftekhim	+	+		+	+									
Novokuibyshevsk oil refinery			+											
Angarsk petrochemical company			+											
Volgogradneftepererabotka	+													
Permnefteorgsintez	+													
Gazpromneft-Omsk oil refinery							+							
Neftekhimik Prikarpat'ya								+						
Pavlodar oil refinery	+		+			+			+					
Atyrau oil refinery									+	+				
Turkmenbashi Complex											+			
Novo-Bakinsky oil refinery														+
Uzneftepererabotka												+	+	

Source: "InfoMine"

I.2. Methods of obtaining green and calcined petroleum coke

Coking of petroleum is the most strict form of thermal cracking of petroleum residues, which is conducted at low pressure and temperature of 480-560°C to obtain petroleum coke, as well as hydrocarbon gases, petrol and kerosene-gas-oil fractions. Coking provides breaking all components of the resources to obtain liquid distillate fractions and hydrocarbon gases; destruction and cycling hydrocarbons with intensive release of kerosene-gas-oil fractions; condensation and polycondensation of hydrocarbons and deep compression of high-molecular compounds with forming massive coke residue.

Industrial process of coking is conducted at facilities of 3 types: periodical coking in coke stills, delayed coking in chambers, continuous coking in pseudo-liquefied layer of coke-carrier.

In the CIS, petroleum coke is obtained by delayed coking and coking in coke stills.

Delayed coking

Delayed (semi-continuous) coking is the most widespread method in the world. Resources, preliminarily heated in tube furnaces up to 350-380°C, is continuously fed to cascade dishes of rectification column (working at atmospheric pressure) and contacts with vapors, rising from reaction apparatus. As a result of mass- and heat-exchange, a part of vapors is condensed, forming with initial resources so-called secondary resources, which are heated in tube furnaces up to 490-510°C and goes to coke chambers – vertical cylindrical apparatus 3-7 m in diameter and 22-30m high for 24-26 hours, where the reaction mass is coked. After filling the chamber with coke by 70-90%, the accumulated coke is removed from the chamber, usually by water jet under high (up to 15 MPa). Coke goes to crushing to lumps maximum 150 mm, and then is screened to fractions 150-25, 25-6 and 6-0.5 mm. The chamber is heated by steam and vapors from operating coke chambers, and is filled with coking mass again.

Volatile products of coking, being vapor-liquid mix, are discharged from operating chambers and separated consequently in the rectification tower, water-separator, gas block and evaporation column into gases, petrols and kerosene-gas-oil fractions (see Table 4).

Table 4: Yield of products at a delayed coking unit, mass %

Product	Raw material		
	Fuel oil (density 0.950 g/cm^3)	Tar (density 0.991 g/cm^3)	Cracking-residue (density 1.024 g/cm^3)
Coke	14-15	23-24	34-35
Gases	4-5	6-7	7-8
Petrols	7-8	15-16	6-7
Kerosene-gas-oil fractions	68-69	58-59	46-47

Source: "InfoMine", data of the enterprises

Typical parameters of the process are as follows: 450-480 ^{o}C, pressure 0.2-0.6 MPa, duration up to 48 hours.

Advantage of the delayed coking is high yield of low-ash coke. The method yields in 1.5-1.6 coke more than continuous coking (from the same amount of resources).

Russian oil refineries exploit one-block and twin-block DCU (each block includes 2-3 reactors) DCU are designed by Institutes Giproneftezavody and VNIPIneft. DCU are classified by yield of finished product.

Twin-block DCU are subdivided into 4 types.

1. DCU equipped with reaction chambers with inner diameter of 4.6m and heating furnaces of hat type. The DCU includes device of absorption and stabilizing of petrol, they also yield kerosene, gas-oil, furnace fuel, heat of which is used for heating. 4 chambers operate in pairs, independently of each other (each pair can be switched off for repair independently).

2. DCU of type 21-10/3M of similar design, with reaction chambers with inner diameter of 5.5 m. The DCU use direct distilled petroleum residues, added with high-aromatic components (aromatization of the coking resources promote increasing yield and grade of coke and prolongs service-life of DCU.

3. For 1975-1990, a number of oil refineries commissioned twin-block DCU of type 21-10/6 (6M). The DCU are equipped with high-efficient equipment: reaction chambers from alloyed steel of 5.5m in diameter and 27.6m high (operating at pressure up to 0.6 MPa); tube furnaces of volume flame for heating initial resources and heat-carrier and vertical-torch furnaces (for heating secondary resources (with bottom position of burners. Three reactive levelers, installed at the reactor, register level of phase separation (coke-foam) that allows to optimize utilization of chamber space.

Increasing efficiency of the DCU operation is reached also at the expense of use of air-cooling facilities as condensers and deep utilization of exhaust heat. Decreasing temperature of secondary resources heating and decreasing coke precipitation is reached at the expense of heating primary resources (heavy coking gas-oil) up to 515^{o}C is special twisted tube. To depress foam formation, special anti-foaming reagent is fed to top zone of chambers. Coke precipitation is prevented by supply of cooled coking gas-oil. Besides, scheme of catching products of chamber heating, steaming and coke cooling was modernized.

4. Reaction chambers of DCU 21-10/5K has a diameter of 7 m, height of 29.3 m. Besides modernizations, applied at previously built DCU, this facility has axial feeding resources into reaction chamber, coke-removing hydraulic complexes with remote control of cutters, electric-driven valves at transfer pipelines, mechanization of labor-consuming processes, coke warehouse of floor type.

The main characteristics of delayed coking units of various types, applied in the CIS, are presented in Table 5.

Table 5: Basic characteristics of different types of delayed coking units, applied at CIS oil refineries

Parameters	Type of unit				
	21-10/300	21-10/600	21-10/3M	21-10/6	21-10/5K
Production, '000 tpy					
by raw material	300	600	600	600	1500
by green coke	75	100	120	120	250
Temperature of reactor, ^{o}C					
top	450	450	450	450	450
lower part	475	475	475	475	475
Pressure of reactor, MPa					
top	0.18	0.4	0.4	0.4	0.4
lower part	0.38	0.6	0.6	0.6	0.6
Height of reactor filling, m	18-20	16-19	17.5	17	19
Cycle duration, h	48-120	68-112	60-99	84-154	-
Inner diameter, mm	5000	4500	5500	5500	7000

Source: InfoMine, data of companies

In the CIS, the most widespread DCU are of types 21-10/300, 21-10/600 and 21-10/3M. Notice that DCU coke is inferior of that of still coke in increased moisture (by 2% in average) and content of volatile components (by 1-2%).

Periodical coking

The process is conducted in horizontal cylindrical apparatus 2-4 m in diameter and 10-13 m long. Resources in a still are gradually heated from the bottom by open fire. Then distillates are separated by common way, coke is heated and calcined (2-3 hours). Then temperature in the furnace under the still is gradually decreased, and the still is cooled by steam and then by air. After cooling coke to 150-200^{o}C, the product is unloaded from the still.

Typical parameters of the process: 360-400^{o}C, atmospheric pressure. This method yields electrode and special high-grade types of coke with low content of volatiles. However, the method provides low productivity, requires large consumption of metal and fuel and manual labor, and, in this connection is not practically used in industry. This method is not used at all abroad and yields around 1% of coke in the CIS (from "InfoMine" estimate).

Continuous coking in fluidized bed

(Thermo-contact cracking)

Raw materials, preliminarily heated in heat exchanger, contact in reactor with heated inert heat-carrier and is coked at its surface for 6-12 minutes. As the heat carrier, usually powdery coke is used with particle size up to 0.3 mm, rarely more. The formed coke and the heat-carrier are removed from reaction zone and are fed to regenerator (coke heater), where in air flow, maintaining the heat-carrier in suspension, up to 40% of coke are burned, and the bulk is supplied to customers. Heat, generated from burning a part of coke, heats the carrier, which is returned to the reactor by pneumo-transport by steam or gas flow. Distillate fractions and gases are removed from the reactor and are separated by the same way as at the delayed coking process.

Typical parameters of the process: temperature in the heat exchanger 300-320°C, in the reactor - 510-540°C and in the regenerator 600-620°C, pressure in the reactor and the regenerator 0.14-0.16 and 0.12-0.16 MPa, respectively, resources/heat-carrier ration (by mass) – (6.5-8.0):1.

Coking in fluidized bed is applied for increasing production of light petroleum derivatives. Besides, combination of continuous coking with gasification of formed coke can be applied for obtaining diesel and boiler fuels.

Calcination

Before use petroleum coke is usually subjected to refining, including several processes. Calcination removes volatile components and partially heteroatoms (for instance, sulfur and vanadium), decreases electric resistance. Graphitization provides ordering structure up to three-dimension ordering of coke. In general, stages of coke refining can be presented by the following scheme:

Crystalline components → carburization (calcinations at 500-1000°C) → two-dimension ordering structure (1000-1400°C) → pre-crystallization (transformation of crystalline components at 1400°C and above) → crystallization or graphitization (2200-2800°C).

Green coke calcination is conducted at CIS oil refineries in rotary, hearth, and chamber ovens of various producibility (Table 6); at the present time, in the CIS, there are 6 oil refineries and JSC Plant Slantsy (Zavod Slantsy), having units on coke calcinations. However, the bulk of coke is calcined by customers themselves: at aluminium smelters (11 furnaces) and electrode plants (3 furnaces).