

Thermal Adsorption Processing Of Hydrocarbon Residues

Sudad H. Al., Guliaeva N.I.

Abstract: The raw materials of secondary catalytic processes must be pre-refined. Among these refining processes are the deasphalting and demetallization including their thermo adsorption (or thermo-contact adsorption) variety. In oil processing four main processes of thermo-adsorption refining of hydrocarbon residues are used: ART (Asphalt Residual Treating - residues deasphalting), 3D (Discriminatory Destructive Distillation), developed in the US, ACT (Adsorption-Contact Treatment) and ETCC (Express Thermo-Contact Cracking), developed in Russia. ART and ACT are processes with absorbers of lift type reactor, while 3D and ETCC processes are with an adsorbing reactor having ultra-short contact time of the raw material with the adsorbent. In all these processes, refining of hydrocarbon residues is achieved by partial Thermo-destructive transformations of hydrocarbons and hetero-atomic compounds with simultaneous adsorption of the formed, on the surface of the adsorbents, resins, asphaltene and carboids, as well as metal-, sulphur - and nitro-organic compounds. Demetallized and deasphalted light and heavy gas oils or their mixtures are a quality raw material for secondary deepening refining processes (catalytic and hydrogenation cracking, etc.), since they are characterized by low coking ability and low content of organometallic compounds that lead to irreversible deactivation of the catalysts of these deepening processes.

Index Terms: Demetallization, Deasphaltization, Adsorbent, Hydrocarbon residues, Lift-reactor, Ultra-short contact time, Catalytic cracking.

1 INTRODUCTION

The long-term trend and the most promising direction of development of world oil refining is to improve the refining processing of raw materials up to 98-100%. This task can be performed only by recycling heavy oil and gas-condensate residues to deepen various catalytic processes (catalytic cracking, hydrocracking, hydro conversion, etc.). However, the catalysts of these deepening processes are extremely sensitive to catalyst poisons (organometallic, sulphur, nitrogen-containing, resin-asphaltic and other compounds) contained in raw materials. Therefore, the raw materials of recycled catalytic processes should be previously refined. The oil refining includes deasphaltization and demetallization processes, including their thermo-adsorption (or thermo-contact adsorption) species. Refining (enriching) of hydrocarbon residues in these processes is carried out by thermo-destructive transformations of hydrocarbons and hetero-atomic compounds and the adsorption of the formed resins, asphaltenes and carboids, as well as metal-, sulphur - and nitro-organic compounds on the surface of adsorbents [1-3]. As adsorbents, granular and powdered solid materials are used. In the processes of thermal-adsorption refining asphaltite does not form, as it is formed during the solvent deasphalting process. In modern oil refining there are four well-known process of thermo-adsorption refining of hydrocarbon residues: ART and 3D processes, developed in the US, and ACT processes and ETCC created in Russia.

2 VARIETIES OF THE BASIC PROCESSES OF THE THERMAL ADSORPTION REFINING

2.1 PROCESSES USING LIFT-REACTORS

One of the first processes of these varieties, developed in the oil industry, is the **process ART** (Asphalt Residual Treating), which is a combination of the process of partial evaporation of raw materials and its decarbonisation and demetallization in a fluidized layer of adsorbent. Industrial work with capacity of 2.5 million tons / year for the implementation of this process was put into operation in the United States in 1983. Technology of ART process largely resembles the technology of catalytic cracking process with lift-reactor, but there is an additional unit for the cleaning of flue gases, of adsorbent regeneration, from sulphur oxides. The pressure of this process is about 0.1 – 0.2 MPa, the temperature is 450-550 °C. The raw material evaporates in the lift-reactor with a minimum conversion that allows keeping the hydrogen atoms in liquid products. Thermolabile resinous-asphaltene part of raw materials is adsorbed with partial thermal degradation. The adsorbent, after steam treatment of the hydrocarbons, is regenerated by burning coke and recycled into lift-reactor in which the contact time of the raw material and the adsorbent is slightly less than the contact time of the raw material and catalyst on the catalytic cracking. Vanadium and nickel content in the adsorbent reaches up to 30 g / kg. The spent adsorbent is discharged into the dump, but if necessary and for economic feasibility may be used for the extraction of vanadium and nickel. As an adsorbent with the trade name "ARTKAT" [4], a microspherical inert adsorbent based on kaolin with a low specific surface area (about 15 m² / g) is used. This adsorbent has a good affinity for metals, and asphaltenes. It should be noted that this adsorbent is expensive, and furthermore, in the process of operation, it is subject to destruction due to the presence of large coke deposits, the burning out of which must be carried out at high temperature. Operating experience of ART method has shown that the processing, for example, of the black oil of heavy Arabian crude oil gives total output of light and heavy gas oil of about 70%, hydrocarbons gases C₃-C₄ 3-8%, benzene 13-17%, coke 10-12 %. Total sulphur removal rate reaches 30-50%, but nitrogenous compounds and organometallic compounds are 35-50 and 95% respectively. Coking ability of raw materials is reduced by 65-

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75%. A result of realization the refining process (deasphaltation and demetallization) for a mixture of light and heavy gas oils is a high-quality raw material for catalytic cracking, in which the yield of benzene reaches more than 42% [1].

The process of ACT (Adsorptive Contact Treatment) was developed in Russia, in the All-Union Scientific Research Institute for oil refining in 1980-1990. The technology, hardware design and effectiveness of this process are quite similar to ART process. As an adsorbent is used natural fine-grained kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), which in its characteristics is close to the fluidized bed cracking catalysts, but has minimal catalytic activity, low specific surface area and increased affinity for coke and metals. The process is carried out by the mass feed rate, for the raw material, of 20/h, with a contact time of 0.5 sec and a reactor temperature of 520 ° C. Solid fine-grained adsorbent is circulated between the reactor and the regenerator. In the reactor, upon the contact with adsorbent solid particles, the light components of the raw material are vaporized, and the resinous-asphaltene compounds containing metals, sulphur and nitrogen, are deposited on the surface of these particles. Some of the high molecular components of the raw material are subjected to cracking to form lighter products and coke. Coked adsorbent is steamed off in the desorption zone of the reactor and transported to a regenerator where it undergoes oxidative regeneration. The process of ACT is characterized by a low yield of hydrocarbon gas and benzene (5-6 and 6-8% respectively) and high yield of gas oil fractions (about 80%). From heavy oil, heavy metals are removed by 95-98%; total sulphur by 35-45%; total nitrogen by 50-60%, coking is reduced by 75-80% by weight. The output of coke is up to 125% of the coking capacity of raw materials of Conradson. Heavy gas oil and a wide gas oil fraction with a coking rate of 3.0 and 2.5%, respectively, and a residual content of heavy metals 1.4 and 1.1 g / t appear to be, after preliminary hydro-treating, high quality catalytic cracking feedstock. Light gas oil after the hydro-treating process may also be involved in commercial diesel fuel. The used adsorbent allows completely eliminating the emissions of sulphur oxides from gases regeneration: their residual content is only 20 mg/kg. In the regenerator, metal sulphates are formed, and then sulphur is reduced in the contactor reactor to hydrogen sulphide, the content of which in the gas process reaches 5%[5]. Other adsorbents can also be used in this process [6], for example powdered petroleum coke and pellets of iron ore. However, petroleum coke has low strength and very low porosity, so it quickly breaks down and poorly adsorbs metals from raw materials. Iron ore pellets have high density and strength, but practically do not have porosity. When used, the energy expenditure on the circulation of the adsorbent between the reactor and the regenerator increases and to maintain a fluidized bed therein. Pellets, moreover, poorly adsorb metals from the raw material and formed coke. As an adsorbent, solid waste of brown coal beneficiation can also be used [7], consisting of the following components, % by weight: SiO_2 67.2-79.9; Al_2O_3 16.7-28.3; Fe_2O_3 , CaO and TiO_2 1.5-2.8; Water - the rest. The strength of the adsorbent (before grinding) is 775-800 H, the particle size (0.25-0.80 mm), the true density (2.350-2.500 g / cm^3), the bulk density (1,000-1,050 g / cm^3), porosity (47-61%) and specific surface area (38, 5-42, 4 m^2 / g). This waste is an effective adsorbent for

the refining of hydrocarbon residues, deriving from them up to 22-29% of light fractions, boiled up to 360°C, and 60-62% of residual fractions would be subjected to further processing or used as fuel oil. The main disadvantages of the processes with the lift-reactors (ACT and ART) are the large dimensions and high location of the reaction apparatuses with respect to the zero level, which increase the capital and operating costs and complicate the maintenance of facilities. Their disadvantage is also the excessive duration contact of the raw material with the adsorbent, which leads to the increase in the yield of undesirable products (coke and low molecular weight gases) [8]. Moreover, a broad porous micro-spherical adsorbent based on kaolin (process ART) and powdery kaolin (process ACT) has low mechanical strength [7].

2.2 PROCESSES USING REACTORS WITH ULTRA-SHORT CONTACT TIME

These processes include the **process of 3D** (Discriminatory Destructive Distillation), which was developed by firm "Barco" (USA). It is a hard thermal adsorption cracking in a reaction system with an ultra-short contact time of the circulating adsorbent with the heated dispersed raw materials. The contact time is a fraction of a second. In the process of 3D, a new generation reactor is used, in which an extremely short contact time of the raw material with the adsorbent is carried out in a short horizontal section of a pipe with its subsequent entry into the cyclone separator. The regenerator is a vertically sectioned two-stage device of fluidized bed and interstage refrigerator for the recovery of excess heat from the combustion of coke from the surface of the adsorbent [7]. Due to the exceptionally short contact time, the unwanted secondary cracking reactions are minimized, resulting in higher yields of liquid products with low coking and low metal content at lower yields of coke and hydrocarbon gas [2, 3, 8].

ETCC process (Express Thermal Contact Cracking)

In terms of its technological and technical nature, it is identical to the 3D process and is intended for decarbonization and demetallization of hydrocarbon residues without significant degradation using a reactor system with an ultra-short contact time. As for hardware design, the system is similar to the system for implementing millisecond catalytic

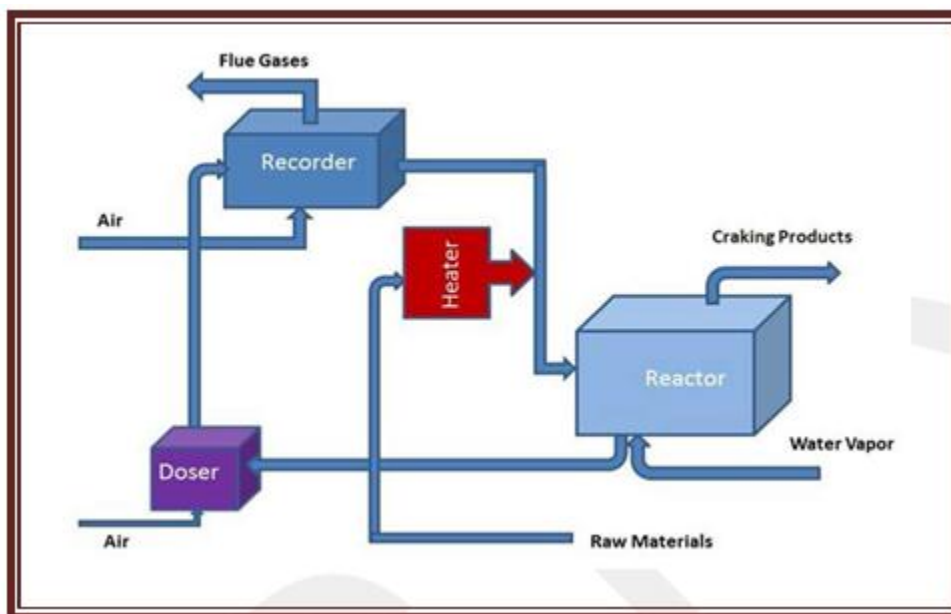


Fig. 1. Process of the express thermal contact cracking

Destructive-adsorption express thermo-contact cracking consists in a short-term contact in a cyclone type reactor at a temperature of 510-530 ° C of a finely dispersed heavy residue with an adsorbent and subsequent oxidative regeneration of coked adsorbent in a horizontal-sectioned regenerator with a fluidized bed [3, 4]. As an adsorbent, pulverized and powdered natural metallic and non-metallic materials and the wastes of their processing (burnt rock, iron ore concentrate, pyrites calcination cinder, kaolin), as well as spent catalyst for cracking are used. In the reactor, an easy conversion is carried out. This conversion represents demetallization and partial decarbonization with the predominant formation of a wide gas oil fraction (heavy gas oil) with a coking ratio of 3% and a metal content of 1.0-1.5 mg / kg, directed to catalytic processing into motor fuels (catalytic cracking and (Or) hydrocracking). When used as adsorbent, the natural fine grained iron ore materials (iron ore concentrate or fines of sulphurous pyrite fuming - waste from the production of sulphuric acid produced during the burning of iron sulphide), may serve as an efficient carrier of sulphur oxides from the regenerator to the reactor, according to the following scheme:

1. Reaction one $\text{FeS} + 2\text{O}_2 \rightarrow \text{FeO} + \text{SO}_3 \rightarrow \text{FeSO}_4$
2. Reaction two $\text{FeSO}_4 + 4\text{H}_2 \rightarrow \text{FeO} + \text{H}_2\text{S} + 3\text{H}_2\text{O}$
3. Reaction three $\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O}$
4. Reaction four $\text{Fe} + \text{RS} + 0,5\text{H}_2 \rightarrow \text{FeS} + \text{RH}$

Reaction (1) takes place in the regenerator, reaction (2) - (4) - in the reactor. As a result of these reactions, the flue gases of regeneration released into the atmosphere do not contain sulphur oxides. The main reaction zone is located in a horizontal pipe into which the injectors supply the amount of raw material proportional to the multiplicity of the adsorbent circulation. The feed is dispersed with water vapour. As a result of contacting the feedstock with the hot adsorbent, hydrocarbon vapours are formed which, in a mixture with steam, transport the adsorbent, at an appropriate rate, along a horizontal tube to its tangential entrance into the primary cyclone. During their joint passage through this tube, reactions

of raw materials transformation with the formation of vapours of reaction products proceed. These vapours also participate in the process of adsorbent transport [9]. When tangentially entering the cyclone, a mixture of vapours with an adsorbent under the action of centrifugal forces is quickly divided into pairs of degradation products (light cracking) and adsorbent particles. The adsorbent particles are poured into the steaming section of the reactor, where steam is stripped off the adsorbent from heavy hydrocarbons. Purified adsorbent particles of reaction product pairs, desorbed hydrocarbons and steaming water vapour are fed through the collecting chamber to separation into a distillation column. The regenerator process is a horizontally sectioned device with fluidized bed, in which the oxidative regeneration of coked adsorbent at a temperature of 600-800 °C [8] is carried out. It consists of two mutually perpendicularly connected vertical and horizontal cylindrical devices. The vertical device serves as a settling zone for separating from the regeneration gases, the adsorbent particles carried by them. To capture fine particles of the regenerated adsorbent at the top of this device, cyclones are installed. The horizontal device serves as the reaction zone of the regenerator in which the oxidative regeneration of the coked adsorbent in the fluidized bed is carried out. To remove the excess heat of the regeneration process and to regulate its temperature regime, the reaction zone is equipped with battery water coolers. The coked adsorbent from the reactor enters the fluidized bed of the reaction zone. The air for burning coke deposits of the adsorbent and creating a stable fluidized bed is fed through the air supply manifolds and the air distribution grate. The flue gases formed as a result of regeneration pass through the separation part of the reaction zone and enter the vertical settling zone of the cylindrical device equipped with cyclones. The fine particles of the adsorbent trapped in the cyclones are returned to the fluidized bed. Purified cyclones regenerate gases are sent to fine purification from dust particles and to heat recovery [9].

3 CONCLUSION

Application of thermal adsorption processes of deasphalting and demetallization of oil and gas condensate residues is a very promising direction of development of oil refining. These processes make it possible to substantially reduce the content of organometallic, resinous, asphaltene, sulphur, nitrogenous and other undesirable compounds in these residues. It make also possible a residue-free and environmentally friendly processing of any hydrocarbon feedstock into high quality motor fuel by catalytic and (or) hydrogenation cracking. Such non-waste production allows achieving the depth of processing of hydrocarbon raw materials at refineries up to 98-100%.

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