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The Influence of Engine Fuel Manufacturing Processes on Their Performance Properties in Operating Conditions

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Additional information is available at the end of the chapter

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1. Introduction

1.1. Straight-run processing of petroleum

Straight-run processing of petroleum (or crude oil) is the kind of processing where the material is distilled after being purified and is separated into fractions (or cuts), based on boiling range differences between its respective components, without modifying the chemical structure of its constituent compounds. Fractional distillation is typically carried out in two steps: under normal pressure and under reduced pressure. Figure 1 shows a simplified diagram for straight-run processing of petroleum.

Before processing, petroleum has a content of solid contaminants (up to 1.5 %) and water (up to 0.3 %). Part of insoluble contaminants and water are removed from petroleum by being left to stand (sedimentation). The process simply involves storage of petroleum in storage tanks for a certain length of time, during which the solids and part of its water content migrate to the bottom while the other solids dissolve in the water, forming a brine, which it is rather hard to remove. In that emulsion, the petroleum is the dispersion medium while water with salts is the disperse phase. Existing emulsion breaking methods are categorized into three groups:

- mechanical methods – involve sedimentation, centrifugation, and filtration of fresh emulsions;

- chemical methods – involving first of all the use of deemulsifiers, which are supposed to dissolve the adsorption film at the water interface;

- electrical methods – involving the use of electrohydrators.
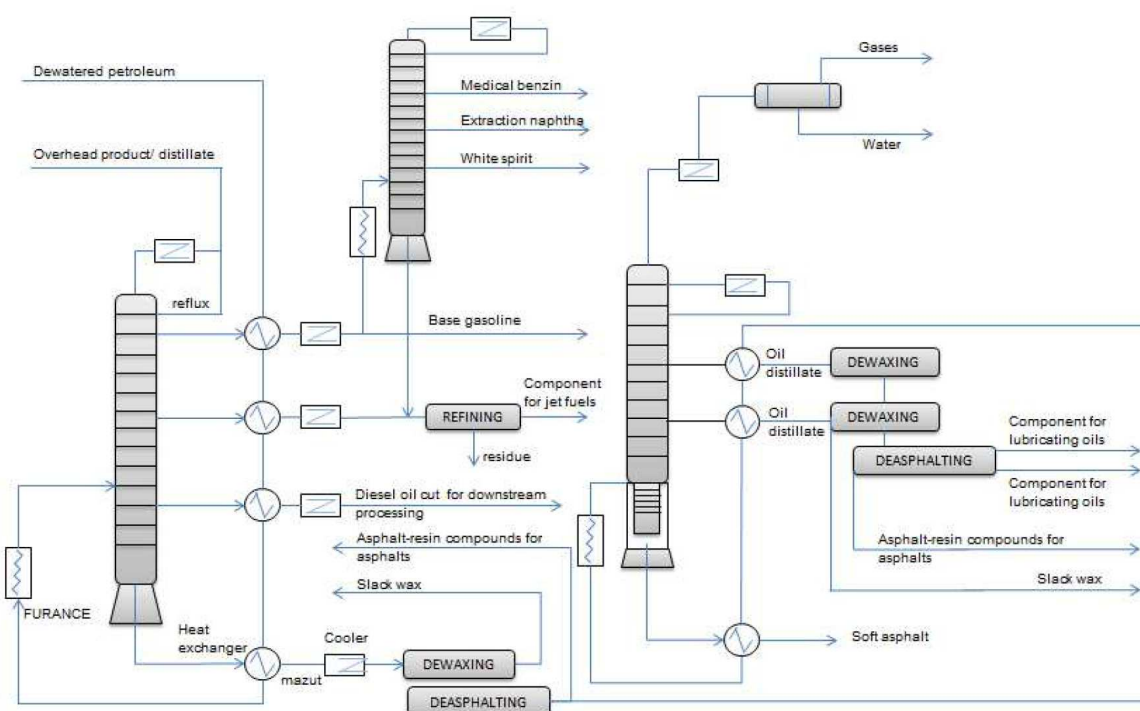
Figure 1. Straight-run processing of petroleum – simplified diagram

In all such groups, deemulsification involves the combining of small disperse water drops by overcoming surface tensions forces at the interface, to form drops big enough to be able to fall down the tank by gravitation. In industry, electrical methods are typically used, where the reactor has two flat electrodes installed in it, between which there is a voltage of about 30 kV. The water molecules move towards the respective electrodes and, as the electrode symbol changes, the molecules lose their electrical orientation and collide with one another, forming suitably large drops which fall down the tank. The resulting dewatered petroleum is taken at the top of the reactor. Electrohydration is carried out at an elevated temperature in a continuous manner.

The purified and degassed petroleum is made to flow into a tubular furnace to be heated to a temperature not higher than 370°C and then to the base of a first distillation tower (atmospheric column). The distillation tower is approximately 40 m high and comprises a number of so-called trays. Their shape depends on the rectification process parameters, the typical tray designs include: bubble cap, sieve, wave, West, cascade, Venturi, ejector, valve, and combinations of the above. The rectification process in the atmospheric tower is carried out at nearly-atmospheric pressures. After flowing into the tower, the hot petroleum is divided into fractions as follows: the consecutive fractions (in terms of density) evaporate and then condense on the respective tray groups, are then taken to heat exchangers (where their heat is transferred to the petroleum flowing into the furnace) and sent downstream.

Inside the column, there circulates a so-called "reflux", which may be of the hot (water or, less frequently, feedstock), cold, or circulating type. The reflux is supposed to keep sufficient temperatures, especially in the top regions of the column.

The products obtained in the atmospheric distillation tower include:

1. overhead fraction (which also functions as the circulating reflux;

2. side fractions (their amount and boiling ranges depend on the process parameters and design of column); typically, they include:

   - light gasoline fraction;

   - naphtha fraction;

   - kerosine fraction (jet fuels);

   - diesel fuel fraction;

   - spindle oil fraction.

3. distillation residue, also called mazut.

For a better fractionation of the gasoline fraction (to obtain medical benzin, extraction naphtha, painter's naphtha), it is possible to re-rectify a portion on it in a separate atmospheric tower. Its design and processing regime are the same as described earlier. Distillation residue from that column is combined with the kerosine fraction. Rectification in each atmospheric tower takes place above the feed point for the gas phase but below the feed point for the liquid phase. In order to ensure appropriate rectification of the liquid phase, it is necessary to provide additional heat or another evaporating agent. Rectification in atmospheric towers is a continuous process.

A vacuum tower is another major component of a straight-run petroleum processing plant. It serves for distillation of the high-boiling distillation residue from the atmospheric tower, after heating it to 430°C in deep-vacuum conditions. In the vacuum towers of to-day, pressures in the evaporation region are in the range (1.99...2.27) kPa, compared with 0.66 kPa at the vapor outlet point. Atmospheric towers are 15-30 m high, their diameter is a max. of 12 m. The column is filled with bubble cap or sieve or valve-type trays; depending on the kind of product made in the vacuum column, the number of trays varies between 8...14 (if the product is used for catalytic cracking) and 38...42 (if the distillate is used for oil production).

Mazut, which flows into the column typically above tray 6, is combined with foam reducers (for instance, silicones at a concentration of 0.75 mg/dm^3 of feedstock). Lower pressure, which is reduced by means of a system of so-called ejectors and condensers, leads to lower boiling ranges, enabling rectification of heavy mazut without decomposing it.

The vacuum tower products include: between one and three side fractions, a gas overhead fraction and the distillation residue called soft asphalt. After further straight-run or destructive processing, the side fractions are an important component for various engine oils and heating oils.

In addition, straight-run processing comprises a number of auxiliary treatments, enabling the various components to be separated from the distillation products. Such treatments include: crystallization and filtration, refining with the use of H_2SO_4 and selective solvent, dewaxing with the use of selective solvents and de-asphalting with propane.

Crystallization and filtration are intended to separate paraffins from the distillation cuts. The crystallized paraffins are then filtered off using a pressure press and filtration cloth. After the removal of paraffins, the oil fraction is further processed and the crude paraffin that results is used for making insulation materials, maintenance materials, or candles (after refining). Refining of the post-distillation fractions is intended to remove asphalts and resinous compounds, which are undesirable in further processing.

1.2. Chemical refining

In order to remove acid oxygen-based compounds or some sulfur compounds, the petroleum products are subjected to refining by means of lye: it reacts with acidic compounds, forming respective water-soluble salts. Part of the compounds remain in the refined product and can only be removed therefrom by washing with water. The oils are refined using weak sodium hydroxide solutions. The process is carried out at elevated temperatures to prevent the formation of emulsions which it would otherwise be hard to break.

In the process of neutralization of the oil distillates with lye, the napthene acid content of the distillate initially reacts with sodium hydroxide to form soaps, which dissolve in aqueous lye solutions whereby they are removed from the distillate; the emulsions formed then are usually not very stable. Stable emulsions are formed after another water-washing operation. This is due to the presence in the oil of resinous products which, in a dispersed form, are hydrophobic emulsifiers. Owing to the presence of high levels of hydrophilic emulsifiers, their activity as hydrophilic emulsifiers is not manifested during neutralization; on the other hand, when washing with water, the hydrophobic emulsifiers are not separated from the oil along with the waste lye and their effect shows very well. The phenomenon is observed when refining oils having a high content of tars and asphalts and a high content of oxidation products. The hydrophobic emulsions formed then may be separated by heating the distillates to high temperatures, by adding a solution of hydrophilic naphthene soaps, or by treatment with the use of weak solutions of mineral acids, which destroy the emulsifier's interface films.

1.3. Refining with the use of selective solvents

Refining the kerosine fractions with solvents is based on the choice of a suitable solvent which is able to dissolve in different ways the desirable and the undesirable components of the refined product. Selective solvents are expected to be able to readily dissolve, to be selective and stable, to form readily separating extract and raffinate phases, to be easily regenerated, to resists corrosion in operating conditions, and to have non-toxic properties.

The essential parameters which determine the level of refining include temperature and the solvent-to-material ratio. The choice of temperature for the refining process depends on the critical temperature of solubility for a given mixture. Refining with the use of selective solvents is feasible in those temperature ranges where a two-phase system exists: the raffinate solution (containing a trace amount of solvent) and the extract solution (comprising mainly the solvent and the undesirable components of the starting raw material which are dissolved in the solvent). The critical solubility temperature depends on the structure of hydrocarbon mole-

cules: their critical solubility temperature is lower (and going down rapidly) for higher numbers of rings in the hydrocarbons but is lower for longer alkyl lengths. Naphthenes with five-member molecules will better reduce the critical temperature of solubility, compared with six-member molecules. In the case of aromatic hydrocarbons and naphthenes with same structures, for same solvent, critical temperature of solubility of aromatic hydrocarbons is much lower than that of naphthenes. Naphthene-aromatic hydrocarbons have lower critical temperatures of solubility, compared with naphthene hydrocarbons having a similar structure. Normal paraffins have the highest critical temperature of solubility. The value of critical temperature of solubility and kerosine fractions in a solvent is affected also by the solvent's properties: for instance, critical temperature of solubility of hydrocarbons in nitrobenzene is much lower than that in phenol, but is lower in phenol compared with that in furfurol.

Solubility of substances in solvents depends on attractive forces between the molecules of the solvent and the solute. Attraction between molecules takes place due to the Van der Waals forces and hydrogen bonds. In view of the fact that kerosine fractions comprise mainly nonpolar hydrocarbons, selective extraction of undesirable components is only possible in the case of Deby's effect, that is, co-operation of induced dipols which are formed in non-polar molecules under the effect of the electric field of polar solvent's molecules. The highest polarizability is shown by aromatic hydrocarbons, the lowest by naphthenes and paraffins. Therefore, aromatic hydrocarbons readily submit to the action of the electric field of solvents, which leads to the formation in their molecules of an induced dipol moment, resulting in their readily dissolving in polar solvents.

In addition to the refining temperature and type of solvent, the degree of extraction of undesirable components depends also on its amount that is indispensable for extraction. On the other hand, the amount of solvent depends on its properties, chemical composition of the starting material, the desirable refining degree, and on the extraction method.

Selective refining by means of furfurol is a method for removing aromatic hydrocarbons from vacuum petroleum distillates, and is used as a base oil production step. Furfurol is a polar substance with a high dipol moment. It is able to selectively dissolve hydrocarbons by inducing the dipol moment in the hydrocarbon molecules which are contacted with furfurol. It is useful as a solvent in selective refining processes because of the following advantages:

- high density and lack of tendency to form foams or emulsions; these properties facilitates phase separation between the raffinate extract solutions;

- low freeze point: therefore, its mixtures are easier to handle at low temperatures, requiring no extra care or devices;

- large difference between the critical temperatures of solubility for paraffinic and aromatic compounds.

On the other hand, furfural has the following disadvantages:

- low resistance to oxidation at high temperatures, both in alkaline and acidic environments,

- formation of acidic oxidation products and high-molecular products of polycondensation;

- high toxicity.

In the process of selective refining with furfurol, aromatic compounds are removed from the oil more readily than paraffins, compounds with high viscosity. Hence, a more aromatic compound requires less solvent and lower temperatures to be entirely dissolved. Therefore, by selecting suitable extraction temperatures and solvent-to-material ratio, it is possible to remove either only aromatic compounds from the raw material or – after modification of extraction conditions – to remove mixed compounds as well.

1.4. Refining by adsorption

Adsorption as a refining process is currently used, first of all, in the finishing of light kerosine cuts, lubricating oils, specialty oils, and paraffins.

The role of adsorption in the refining of petroleum products is in the adsorption of asphaltenes, resins, diolefins, acids, etc. on the adsorbent surface, consequently providing a finished product with improved color and odor, and stable physico-chemical and performance properties.

The adsorption refining process is carried out either by the cold or hot method, using percolation (where adsorbent pellets are used) or by the contact method, using so-called decolorizing earths (adsorbents in the pulverized form, obtained from natural aluminosilicates).

The following materials are used in the refining process:

- sorbents, obtained by thermal or thermal-chemical modification of natural mineral raw materials (aluminosilicates);

- synthetic sorbents, such as: silica gel or alumina;

- active carbon.

When selecting s suitable sorbent, care is taken not only about the efficiency of regeneration, connected with improving the properties of oil, but also about the cost-efficiency of the process. To select the most suitable sorbent, it is necessary to consider some of its properties, first of all, its refining capacity, selectivity, chemical properties, mechanical strength, costs, availability, possible reactivation, and disposal.

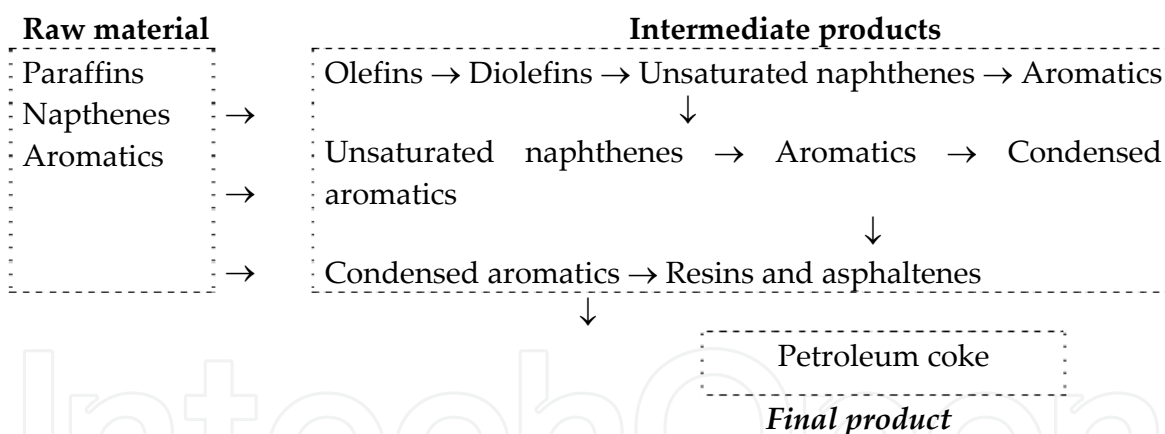## 2. Destructive processing of petroleum

Destructive processing of petroleum involves modification of the structure of hydrocarbons contained in the fractions obtained from the straight-run processing of petroleum. Such modification is intended to improve intermediates for use in final product blending. Destructive processing cannot be carried out with the omission of straight-run processing. The essential process groups included in destructive processing of petroleum are discussed below.

2.1. Thermal cracking

Thermal cracking is a process in which large hydrocarbon molecules are broken to form light unsaturated hydrocarbons in high-temperature conditions.

Thermal cracking comprises three groups of processes:

• Cracking of liquid raw materials at high pressures (1961.3...6864.6) kPa in the temperature range (470...540)°C to obtain gasoline. The process is intended to obtain a higher amount of fuels at the cost of oil fractions. Gasoline can be obtained from the post-distillation side-fractions in atmospheric and vacuum towers, while heating oils can be obtained from the distillation residue (soft asphalt) in a vacuum tower. The process to obtain heating oils, carried out in mild conditions, is called *visbreaking*;

• Low-pressure cracking – also called coking, or destructive distillation. The process is carried out at temperatures in the range (450...550)°C. It is intended to provide light-colored products with a high hydrogen content, such as gasoline, diesel fuels or gases, as a result of decarbonization (concentrating asphalts and resins into so-called "petroleum coke"). The coke product is often a target product, intended for making, for instance, coatings for electrodes. The coking process is carried out as shown in the diagram below and may be interrupted or slowed down at any time by injection of an extra amount of cold raw material.

Raw material	Intermediate products
Paraffins Naphtenes → Aromatics → →	Olefins → Diolefins → Unsaturated naphthenes → Aromatics ↓ Unsaturated naphthenes → Aromatics → Condensed aromatics ↓ Condensed aromatics → Resins and asphaltenes

↓

Petroleum coke

Final product

• Thermal cracking in the most severe conditions: pyrolysis. The process is carried out at temperatures in the range (670...800)°C (though the process temperature may be as high as 1200°C). The process is intended mainly to provide unsaturated gases, usually ethylene, for use in petrochemical syntheses. The process also provides aromatic hydrocarbons such as benzene, toluene, xylenes, or naphthalene, and so-called post-pyrolytic gasoline which is a component for automotive gasoline, though they are only to be considered as side products.

In addition to the above, there exist a number of intermediate thermal cracking processes, for instance, vapor phase cracking in low pressure conditions at a temperature of 600°C to produce gasoline, or coking of the residue in severe conditions in order to increase the amount of gas and aromatization of liquid products.

2.2. Catalytic cracking

Catalytic or thermocatalytic cracking processes are carried out at high temperatures in the presence of catalysts. They are intended to provide light products with good quality at the cost of heavy products (mainly gasoline and diesel fuels) or to improve the quality of other distillation products.

Gasoline and diesel fuels, obtained at temperatures in the range (450...500)°C in the presence of an aluminosilicate catalyst, are characterized by high resistance to decomposition and oxidation processes (mainly gasoline) and high purity. The mechanism of catalytic cracking is reverse to that of thermal cracking and leads to highly saturated hydrocarbons.

Gasoline reforming has been isolated from the catalytic cracking and is a separate process, intended to improve the gasoline fractions by their aromatization and purification to remove sulfur compounds therefrom. Pure aromatic hydrocarbons such as benzene, toluene, xylenes, can be obtained from the aromatized gasoline for petrochemical synthesis after its suitable separation. Moreover, reforming provides hydrogen for hydrogen processes. Depending on its variant, the reforming process uses a number of catalysts (Co, Ni, Mo, Pt, Fe), usually aluminosilicates. The process temperature is around 550°C. The essential reactions taking place during gasoline reforming include dehydrogenation of cycloalkanes (naphthenes), dehydroi-somerization of naphthenes, and dehydrocyclization of alkanes (paraffins). These reactions are accompanied by isomerization and hydrocracking of paraffins. The essential reactions generate free hydrogen, therefore, such reactions as desulfurization and saturation of alkenes take place as well.

2.3. Fluidized-Bed Catalytic Cracking

Fluidized-Bed Catalytic Cracking (FBCC) of de-asphalted vacuum and heavy petrolum cuts, in the presence of aluminosilicate catalysts (typically zeolites), is one of the major methods for deep processing of petroleum that are used in advanced refineries. The process is highly complex in terms of equipment and, accordingly, involves relatively high investment costs. On the other hand, the use of the process unit is justified in economic terms, since on average, only about 50 % (m/m) of petroleum is distilled-off at an atmospheric pressure. The petroleum fraction that results from vacuum distillation, having a boiling range of (350...500)°C and constituting typically 25 % of its weight, is a perfect feedstock for the FBCC plant, for making valuable components of engine fuels and light olefins for use in synthetic plastics (polyethy-lene, polypropylene, rubbers, etc).

Cracking of high-molecular hydrocarbons causes breaking of intermolecular bonds, which is accompanied by dehydrogenation and hydrogenation, comprising hydrogen transfer reac-tions. The bonds between carbon atoms are broken in irreversible reactions. Out of a great variety of bonds between the atoms, those with the lowest energy are the easiest to break. The elementary energy of C-C bonds in paraffins is 265 kJ/mol, for C-H bonds it is 360 kJ/mol, and that of C-C bonds in aromatic compounds is (500...610) kJ/mol, therefore, paraffins are most frequently subjected to cracking. Hydrogen transfer reactions contribute to the formation of gasoline compounds as saturated compounds, though at the cost of formation of those with a

low hydrogen content, including coke. During the cracking process, owing to thermodynamic conditions, polymerization of olefins – though only insignificant – is the first phase in the formation of aromatic compounds and coke.

The essential reaction leading to the formation of coke is the condensation of aromatic hydrocarbons with olefins. Therefore, naphthenes and naphthene-paraffin compounds are the most preferable raw materials for fluidized-bed cracking. On the other hand, aromatic feedstock hinders the cracking process, favoring the formation of coke.

During the cracking process, primary reactions are accompanied by a number of secondary ones which become more and more intensified: such processes include polymerization, aromatization, isomerization, alkylation and dealkylation. Catalytic cracking takes place at lower temperatures, compared with thermal cracking but the amount of coke being formed in it is much more limited. The aluminosilicate catalysts used in the process accelerate the most desirable reactions: the rate of cracking of paraffins is 10 times as high, compared with that in a purely thermal process, conversion of naphthenes is 1000 times as fast, and that of side-chain aromatics is 10,000 times as fast.

The cracking feedstock contains more or less of metals (mainly vanadium, nickel, and iron), sulfur and nitrogen, in addition to oxygen. Organometallic links are broken and their metals accumulate on the catalyst, leading to its deactivation, accelerated formation of coke, and higher amount of gaseous hydrocarbons.

Cracking of aromatic feedstock is characterized by an increased efficiency of the formation of aromatic hydrocarbons with a considerable admixture of olefins, in addition to the higher amount of coke. A naphthene feedstock produces a top quality gasoline as the result of isomerization and aromatization reactions.

A fluidized-bed catalytic cracking plant is composed essentially of a vertical-tube reactor, raising the catalyst and raw material (the basic process zone) and a regenerator with pipes carrying a spent and regenerated aluminum-silicon oxide system. At the bottom of the vertical tube, the strongly pulverized catalyst is mixed with the – nearly entirely evaporated – heavy hydrocarbon feed; cracking takes place as the feed flows upwards at the rate of (4...12) m/sec at a pressure in the range (0.8...1;5) bar, at a temperature typically in the range (480...530)°C. The cracking of heavy petroleum feedstocks is accompanied by the formation of coke: it accumulates on the catalyst, blocking its active sites. In such conditions, it is gravitationally carried into a regenerator to remove the coke by burning, typically at temperatures in the range (635...650)°C.

The naphtha cut from the FBCC plant is the main source of sulfur being carried into the final gasoline products during the blending process. In the global refinery industry, the level of sulfur in nahptha obtained by FBCC is reduced by the following methods:

- pre-treatment of the FBCC feedstock using a hydrogen-catalyst method for the removal of the entrained sulfur;

- increasing the conversion of organic sulfur compounds into hydrogen sulfide during FBCC;

- processing the FBCC product by distillation with absorption.

The highest percentage of sulfur is concentrated in the highest-boiling gasoline fraction from FBCC. Therefore, lowering the final boiling range of that fraction is the obvious method to reduce its sulfur content. The available techniques include the following:

• dropping part of naphtha into light diesel fuel; on the other hand, rejecting part of naphtha leads to higher quantities of light oil being collected but reduces its boiling range, changes the heat load of the light oil (part of which is recirculated within the main rectifying column) and degrades part of the naphtha to the medium distillate range;

• collecting separately the heavier naphtha cut as part of the overall distillation of FBCC products; however, this changes product proportions, operation of the major fractionating column, and operation of the gas absorption system.

2.4. Hydrogen-based processes

Hydrogen-based processes are thermo-catalytic processes, carried out at free-hydrogen pressure conditions. There are three different variants of hydrogen-based processes, depending on the degree of conversion; only those relating to the production of fuel components will be discussed later in this chapter.

2.4.1. Hydrodesulfurization of the cracking feedstock

A hydrocracking plant usually comprises the following units: hydrocracking of vacuum distillates, hydrogen generation, and hydrogen recovery from post-production gas. The process is intended to handle vacuum distillates from the pipe-tower distillation system with a boiling range (330...575)°C and provide desulfurized products having lower molecular weights and lower boiling ranges.

The process of technology in the plant is divided into the following steps: hydrodesulfurization, hydrocracking, and fractionation of hydrocracking products. Hydrodesulfurization and hydrocracking take place in the presence of catalysts at elevated temperatures (340...450)°C, at a hydrogen pressure of about 15 MPa. The hydrodesulfurization reaction is accompanied by the removal of other contaminants from the feedstock (including nitrogen, chlorine, oxygen, metals), hydrogenation of olefins, and part of aromatic compounds. The main reason why the metals are removed is to protect the catalyst from irreversible deactivation taking place as metal compounds accumulate on the catalyst's surface.

The mechanisms of hydrocracking include two basic conversions: cracking of hydrocarbons, and hydrogenation of the products of catalytic cracking, typically in the presence of an aluminosilicate-based nickel-tungsten catalyst. The post-reaction mixture provides the following fractions: liquid gas, light gasoline, middle gasoline, aviation fuel, light diesel fuel, heavy diesel fuel, and a desulfurized but non-cracked vacuum oil fraction which is a feedstock to the fluidized-bed catalytic cracking (FBCC) plant.

Hydrocracking has the essential advantage of providing top quality products which, unlike similar products obtained by catalytic cracking, have a better stability because they contain no olefins or dienes. Moreover, the content of sulfur and nitrogen in the gasoline and diesel fuel

products obtained is low enough to enable them to be used directly in obtaining environmentally-friendly blends of final products.

2.4.2. Destructive hydrogenation

Destructive hydrogenation is a process in which a solid and a liquid feedstock is cracked under a hydrogen pressure in the range (29419.8...68646.2) kPa at a temperature in the range (420...500)°C in the presence of catalysts (Fe, W, Mo, Ni). The process is intended to produce gasoline products, but sometimes also diesel fuels from coal, bituminous shale, tar and soft asphalt.

2.5. Catalytic processing of gases and light gasoline fractions

The processing of light fractions and gases is intended to provide saturated components of fuels or products for petrochemical syntheses. The process includes the following reactions, running in the presence of suitable catalysts:

- polymerization of gaseous alkenes;

- alkylation of gaseous and liquid isoparaffins with alkenes;

- alkylation of aromatic compounds with alkenes;

- dehydrogenation of butane and pentane fractions;

- isomerization of butane and light hydrocarbons from gasoline fractions.

Although rather energy-consuming, the catalytic processing of these gases enables elimination of distillation losses, that is, flare combustion of gases while increasing the obtained amounts of gasoline.

2.6. Efficient processing of soft asphalt

Soft-asphalt utilization technology includes thermal methods (mainly coking and *visbreaking*), extraction, hydrogen-based methods (such as hydrodesulfurization and hydrocracking), and gasification.

Among these methods, hydrogen-based processes and gasification are believed to have the highest potential and be most environmentally-friendly, although they require the highest investment costs.

Lurgi offers a Multi Purpose Gasification (MPG) technology for gasification of hydrocarbon feedstock. Its main advantages include the possibility to handle low-quality/high-viscosity heavy fractions, also with a content of sludge, mud, and waste coke, and the possibility to handle raw materials with a high sulfur content. The oxygen-steam feedstock gasification unit comprises a burner and a reactor, gas cooling section, and a system for the removal of ash, metals, soot, and liquid waste.

Gasification is an autothermal process, controlled by the oxygen-to-steam ratio, running according to the following reaction:

$$2CH_n + O_2 \rightarrow 2CO + nH_2$$
$$CH_n + H_2O \rightarrow CO + (n/2 + 1) H_2$$
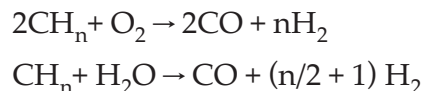
The ratio of CO and H_2 generated in syngas depends on the composition of raw materials, oxygen-to-steam ratio, and parameters of gasification. Non-catalytic semi-combustion of hydrocarbons in the MPG technology takes place in an empty reactor lined with a refractory material, selected for a load resulting from the ash content in the feedstock. The material is fed into the reactor through the burner at the top of the reactor. The burner accepts liquid feeds with the highest viscosities as well as emulsions and sludge with particles the size of several millimeters. The feed and an oxidizer are heated and mixed with steam as a moderator before the burner. The burner and the reactor are "fine-tuned", or adapted, to each other by dynamic simulation to entirely mix the reactants in as small a volume as possible and, in this way gasification of the raw materials is complete. The hot crude gas from the reactor is quenched with water originating from the ash and soot removal unit. The water is injected in a radial arrangement into the quenching-ring zone, where it is quenched, or cooled down rapidly, into the form of glassy beads the size of (1...2) mm. The beads accumulate at the bottom of the separator and are discharged through a hopper. The glassy slag carries a majority of heavy metal content and water-insoluble components. Further cooling takes place in a medium-pressure steam boiler, generating steam in the range (1.5...3.0) MPa. Final cooling takes place in a water cooler, then the gas is sent to the acid gas removal unit.

The crude syngas portion which is intended for use in hydrogen generator, passing by the steam boiler, is sent straight into the CO catalytic conversion unit, working according to the following reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$
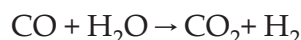
Carbon dioxide is removed by means of cooled methanol.

The syngas, generated during gasification of hydrocarbons, contains a certain amount of free carbon (soot), typically about 0.8 % (m/m) on the feedstock basis. The soot particles are removed from the gas together with ash, mainly in the Venturi gas srubber, located after the quenching section. Sludge with a content of soot is collected together with condensates from the steam boiler and from the cooler-gas scrubber, and is sent to the ash (and metals) removal section. The sludge, with soot from gasification, is depressured batchwise to an atmospheric pressure in the sludge tank before being filtered.

The German refinery PCK Schwedt and Toyo Engineering Corporation from Japan developed one of the most advanced processes of technology for processing the residue from vacuum distillation of petroleum: HSC-DESUS (*HSC-High Conversion Soaker Cracking*). Compared with conventional visbreaking, it is characterized by a very high conversion and the residue has a stable quality. A variety of intermediate products can be used as a feedstock with a high content of sulfur and heavy metals (including heavy oil and bitumens from oil sands as well as residues from the production of lubricating oil). Post-cracking distillates from that technology are

usually light or heavy gas oils having a lower content of unsaturated compounds than that in distillates from coking processes.

In the HSC technology, the feedstock is heated to a temperature in the range 440…460°C, depending on the desired conversion in the soaking drum. Cracking in the furnace is minimized by using high flow rates. A reactant stream from the furnace is made to flow into the soaking drum in which the residence time is long enough to provide desired conversions. The soaking drum operates at an atmospheric pressure, and its bottom section is filled with stripping steam. In the soaking drum, the raw material flows downward, through perforated plates. Steam along with cracking gas and distillate vapor flow through the perforated plates upward; their flow is countercurrent, compared with that of the raw material. The temperature in the soaking drum is highest at the top and becomes lower in its lower sections due to the adiabatic cracking reaction and stripping of the cracked substrate. The liquid from the bottom is pumped out and quenched in the heat exchanger to a temperature of less than 350°C. Vapor from the soaking drum flows into the rectifying column in which desirable intermediate fractions are formed, including heavy vacuum oil.
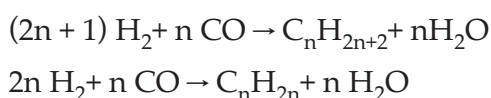
The soaking drum contains a stable homogeneous dispersion of asphaltenes in the residue, even at much higher conversions than in conventional visbreaking.

Distillates from conventional visbreaking, which is regarded as a first step in the processing of soft asphalt, and from the second step (the HSC plant) are then subjected to hydrogen treatment in the DESUS plant. The feed, after a multi-step heat exchange and after being mixed with hydrogen, is made to flow through the furnace and into a fixed-bed reactor. This is the hydrofining reactor, where sulfur, nitrogen, and oxygen are removed from the liquid reactants and hydrocracking takes place, with conversions of around 30 % (m/m). The post-reaction mixture flows through heat exchangers first into the hot separator, then the vapor and gas flow through a heat exchanger and two-step coolers into a cold separator for the separation of the liquid/gas phases. Liquid products are sent downstream to rectification, except that light fractions are subjected to stabilization.
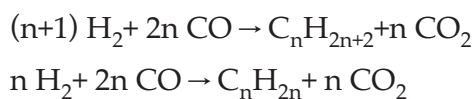
3. Manufacturing of synthetic liquid fuels

The process to make synthetic fuels from syngas is known as the Fischer-Tropsch synthesis and was first used commercially in the 1940's. The process to make engine fuels from a gas which contains a mixture of carbon monoxide and hydrogen, in the presence of cobalt and iron catalysts runs according to the following reaction:

the cobalt catalyst

$$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + nH_2O$$
$$2n\ H_2 + n\ CO \rightarrow C_nH_{2n} + n\ H_2O$$

the iron catalyst

$$(n+1) \, H_2 + 2n \, CO \rightarrow C_nH_{2n+2} + n \, CO_2$$

$$n \, H_2 + 2n \, CO \rightarrow C_nH_{2n} + n \, CO_2$$

The process comprises:

- syngas production by oxygen-steam gasification of coal, or by the catalytic semi-combustion or catalytic reforming (or both processes) of natural gas in the presence of steam;

- removal of sulfur and carbon dioxide;

- catalytic synthesis of carbon monoxide and hydrogen to form hydrocarbons;

- distillation and treatment of the resulting intermediate products to obtain: liquefied gas, gasoline, jet fuels, diesel fuel, and paraffins.

The first American plant using the Fischer-Tropsch technology was built, in 1951, in Brownsville, Texas, by Carthage Hydrocol Company. It was based on a desulfurized natural gas. The plant was composed of two reactors (diameter 5.1 m, height 24 m), packed with 200 Mg of a fluid-bed iron catalyst each. A simplified diagram of the process is shown in Fig. 2. The oxygen generating plant supplied 1800 Mg O_2 per day into the generator of catalytic semi-combustion of methane. The whole process was carried out at 3 MPa. Carbon dioxide was removed from syngas using a water jet.

Water, as a coolant, was made to flow through coolers located in the catalyst bed. Heat, generated during the reaction, was used for making steam. Gas and synthesis products were collected at the top of the reactor, carrying along the fine dust of the catalyst after removing it downstream by means of cyclones. The condensing portion of hydrocarbons and oxygen compounds was chilled and washed out with water. Lighter hydrocarbons were removed using an absorption-desorption system. C_3 and C_4 olefins were polymerized catalytically, obtaining gasoline which was then refined.

The resulting liquid products were composed of 25 % oxygen compounds and 75 % hydrocarbons. Gasoline after final treatment had a high olefin content and its octane number was 85.

In 1955, in Sasolburg, South Africa, a coal-based plant using the Fischer-Tropsch synthesis was started. The raw material, named SASOL, is a poorly-sintering type of coal, containing about 25 % ash and 10 % water, its heat of combustion is 23,000 kJ/kg. Fig. 3 shows a general diagram of the process to obtain synthetic fuels in the Sasolburg plant.

Coal is crushed into finer pieces and then divided into three categories. The smallest pieces are used in the power station in four boilers, each of a capacity of 160 tons of steam per hour. After purification, the gas at a pressure 2.5 MPa is separated into two streams: one stream is sent to the synthesis unit which is equipped with revamped fixed-bed cylindrical reactors (each has a heat exchanger, cooler and blower enabling the gas to be recirculated). The other gas stream is made to flow to fluidized-bed reactors which are supplied with the gas obtained from conversion of the C_1 and C_2 hydrocarbons being made at the same plant. Each reactor in the
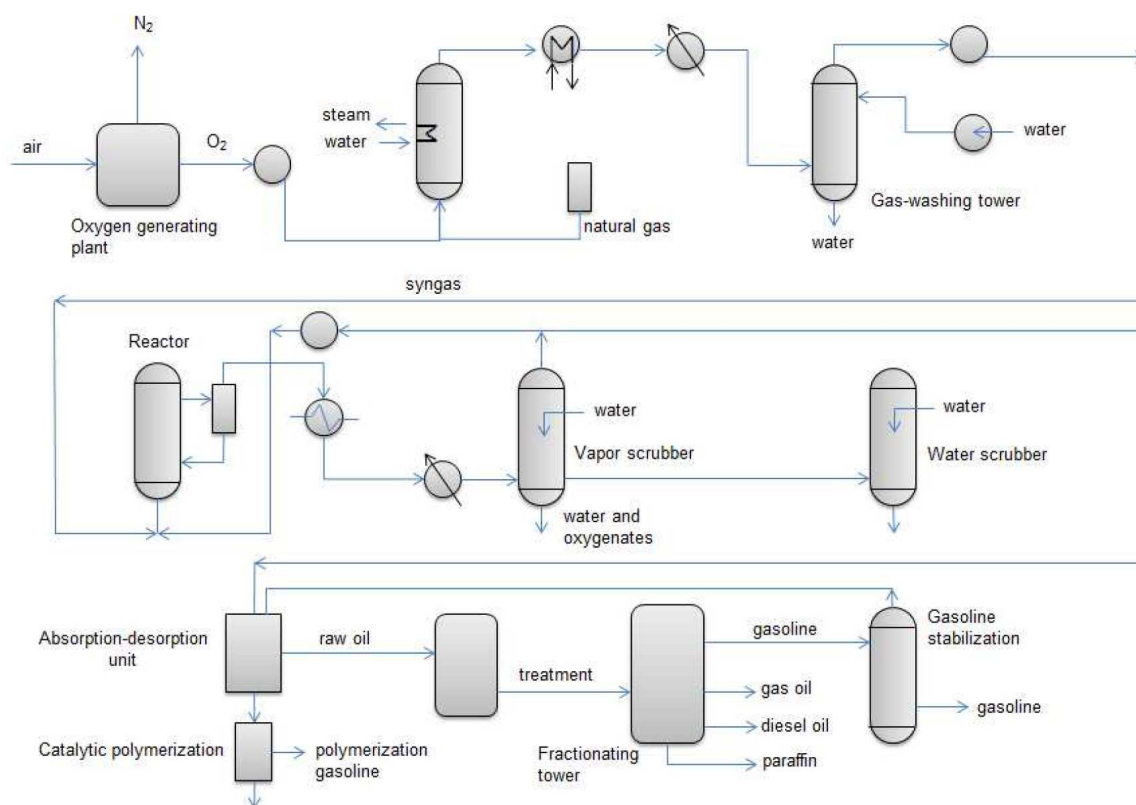
Figure 2. Simplified diagram of the Hydrocol plant.

synthesis plant is provided with approx. 20,000 m³ of syngas per hour. The gas conversion is in the range (50...60) %.

A majority of the products obtained in the synthetic plant are high-boiling hydrocarbons. The fluidized-bed reactors produce mainly gasoline.
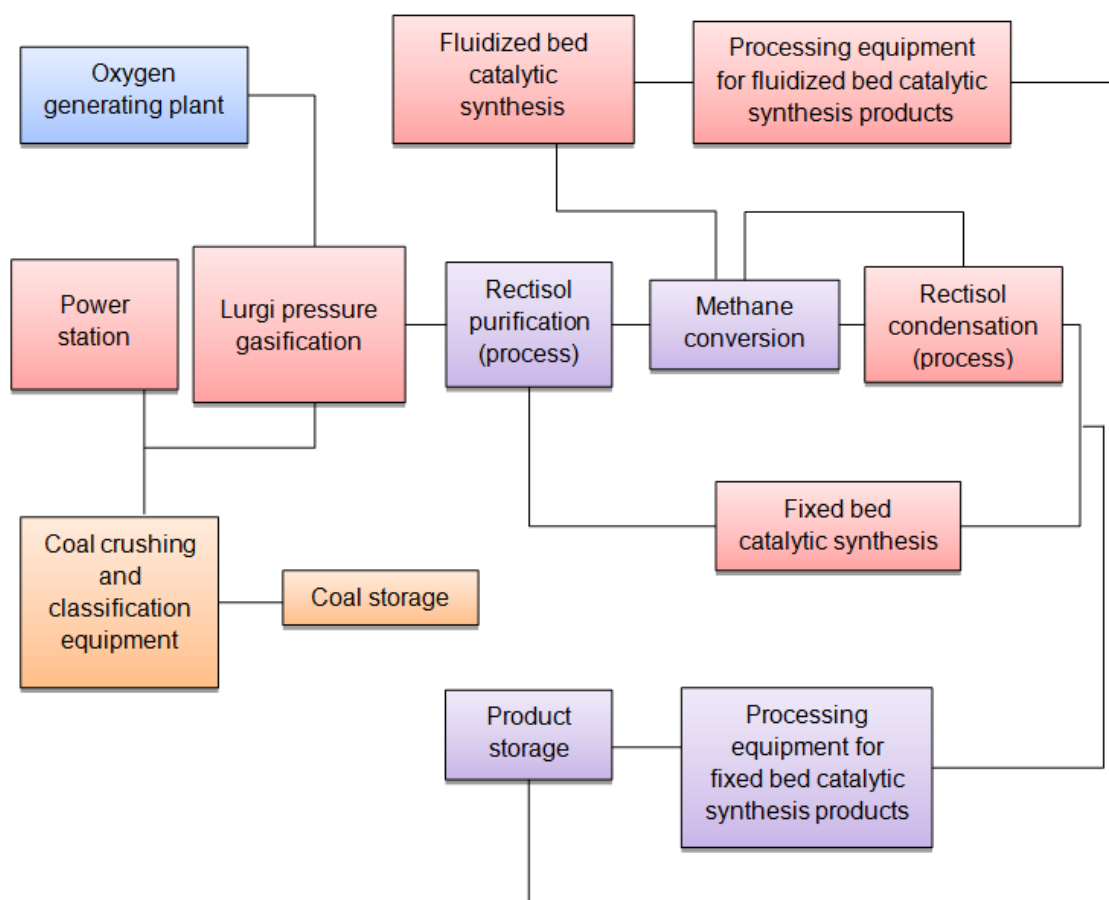
3.1. Methanol as a starting material for making liquid fuels and petrochemical products

At present, the synthesis of methanol is carried out globally starting from a mixture of carbon monoxide and dioxide and hydrogen in the presence of catalysts which typically contain Cu-Zn-Al or Cu-Zn-Cr at a pressure in the range (5...10) MPa at a temperature in the range 240…275°C, according to the following reaction:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \qquad \Delta H^0 = -92 \text{ kJ/mol}$$

and, in part:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \qquad \Delta H^0 = -50 \text{ kJ/mol}$$

Figure 3. A block diagram of the synthetic fuel plant in Sasolburg (source: own elaboration on the basis of company materials)

The process selectivity is enormously high, therefore, only a maximum of 0.5 % (m/m) of side products (in addition to water) is made.

A diagram of the complete methanol plant, based on natural gas or biogas from a municipal waste dump or anaerobic biomass fermentation tanks, is shown in Fig. 4. The methane or biogas is heated in the central furnace to approx. 420°C and made to flow into a desulfurization reactor which is packed with zinc oxide beads ($ZnO+H_2S \rightarrow ZnS+H_2O$). From the reactor, the gas flows into the saturator (scrubber) to be saturated with steam. The saturator is supplied with a mixture of hot water from the distillation section and from the process condensate tank. Methane is heated in the respective apparatuses to about 800°C after being saturated with more steam (live steam) to form the desired mixture, and then directed into the reforming unit I° for the endothermal reaction $CH_4+H_2O \rightarrow CO+3H_2$ to take place on the $Ni/\gamma-Al_2O_3$ catalyst. If a biogas with 60 % CH_4 and 40 % CO_2 is used for the synthesis of methanol, then the reaction $CH_4+CO_2 \rightarrow 2CO+2H_2$ takes place additionally. Approximately 10 % (v/v) of methane is not converted, therefore, the reaction mixture is sent into the reactor II° for a strongly exothermal semi-combustion of CH_4 to take place with participation of a strictly measured amount of oxygen on a nickel catalyst, according to the reaction:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2$$
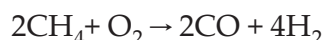
A syngas at nearly 900°C is then made to flow through a boiler which generates compressed steam for the methanol plant, and is combined with hydrogen, separated from fuel gas (post-production gas) by Pressure Swing Adsorption (PSA).
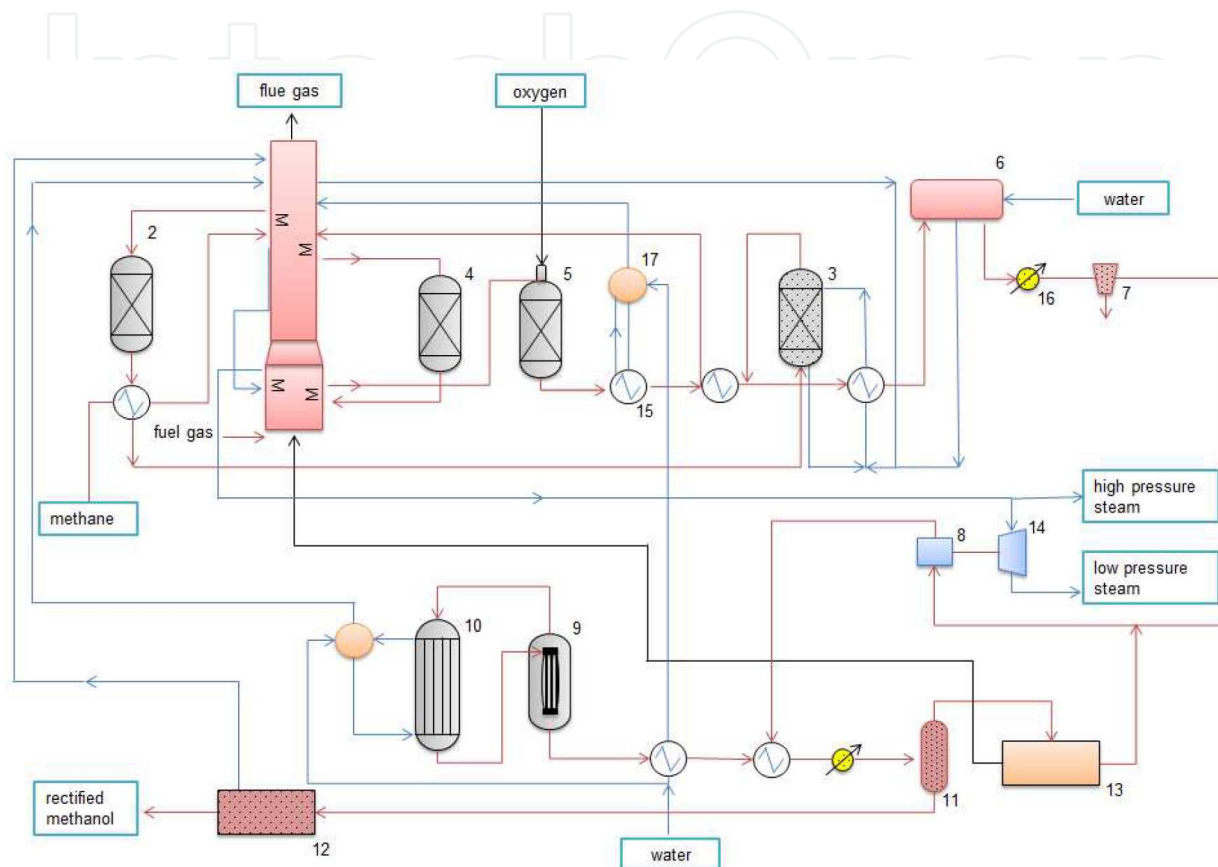
Figure 4. A diagram of the methanol plant based on natural gas or biogas at Lurgi Ől-Gas (source: own elaboration on the basis of company materials) **1** – central gas-fired heater, **2** – methane desulfurization reactor with a ZnO catalyst, **3** – saturator, **4** – stage 1 reactor for methane steam reforming over a Ni catalyst, **5** – stage 2 reactor for methane reforming with the use of oxygen, **6** – water evaporator, **7** – water separator, **8** – turbocompressor, **9** – stage 1 reactor for methanol synthesis, **10** – stage 2 reactor for methanol synthesis, **11** – methanol recovery from unreacted syngas, **12** – 3-column distillation of raw methanol, **13** – hydrogen recovery from waste gases, PSA method, **14** – steam turbine which drives the turbocompressors of syngas and recycle gas, **15** – heat exchanger, **16** – cooler, **17** – water-steam separator

Then, it is sent into the turbo-compressor to obtain a pressure in the range (5...10) MPa and is combined with the unreacted reactant being recirculated from the methanol separator, and sent to two serially-connected methanol synthesis reactors. After the second synthesis reactor, the post-reaction mixture flows through the heat exchanger and water-cooled methanol condenser into the product separator. From the bottom part of the product separator, a crude methanol flows through pressure reduction valves and into three serially-connected rectifying columns. After the last rectifying column in the series, the purity of the methanol product is a minimum of 99.99 %. A portion of the unconverted post-process gas is recirculated for another

synthesis of CH_3OH, while another portion is sent through the PSA system (for recovery of hydrogen) into the fuel gas network and then into the central furnace. Bleeding a portion of the unconverted post-process gas continuously enables the inert content in circulation (N_2+CH_4) to be kept at a stable level of approximately 15 % (v/v). The first step, in which a crude methanol is neutralized using an aqueous soda lye solution, is followed by oxidation of aldehydes and iron cabonyls using an aqueous potassium permanganate solution. This results in the formation of a sludge which comprises manganese dioxide and other solids and is removed by filtration. The crude methanol is refined by distillation in two or three rectifying columns. For a two-column system, two process variants are possible: either both columns operate at an atmospheric pressure, or one operates at an atmospheric pressure while the other does at an elevated pressure.

The components of crude methanol are divided into three essential groups: light components, ethanol, and higher alcohols. Low-boiling compounds, having boiling points lower than or close to that of methanol, are removed along with the dissolved gases from the synthesis plant (H_2, CO, CO_2, CH_4 etc.) in the first column. It is also referred to as the extraction column, with water being the extraction agent, which differentiates the liquid phase activity coefficients of the major components. The scope of changes in the activities of the respective components is determined by the quantity of the solvent required.

The crude feed is pre-treated with chemicals (NaOH, $KMnO_4$), then heated to a boiling range and made to flow into the middle section of the extraction column. Extraction water, which is recirculated from the bottom section of the second rectifying column, is fed to the top of the extraction column. When extracting, the water is cooled down in the heat exchanger by the flowing crude methanol feed. Vapors from the extraction column, flowing upwards, carry along all the volatiles and a small amount of methanol vapor with water. Most of the methanol, water, and of less volatile components are condensed in the condenser and recirculated as the reflux through the separator and into the extraction column, the other ones escape to the fuel gas network or to the flare.

After extraction distillation, the crude methanol from the column bottom contains roughly 50% (m/m) CH_3OH. The volume of the extractant to be added depends on the amount of contaminants as actually found in the crude feed and as shown in product specifications.

The second rectifying column is called the refining column: its main function is to separate water and high-boiling compounds from methanol being the principal product. Higher alcohols have a maximum concentration at the bottom of the column, below the feed point. Therefore, that part of the column comprises alternative points for carrying out higher alcohols from the system. The higher alcohols, if being carried out with the vapor stream, must be cooled down, condensed and sent into the separator. In addition to the higher alcohols and high-boiling components, the stream has a content of methanol, water, and small amounts of ethanol. If the stream is carried out from the lower trays of the stripping section or as a "liquid blow", it may have a significant water content and is likely to become separated into two phases if allowed to stand. The light phase (or the organic phase) is a quite valuable fuel and may be used as a fuel for a furnace (methane reforming reactor, or steam boiler). The aqueous phase may be drained and disposed of as a chemical liquid waste.

In a two-column process system, the pure methanol is collected at the top of the refining column. Typically, it is collected between trays number 4 and 6, counting from the top down. That section has 4 to 6 trays at the top (pasteurization section) and is designed to concentrate low-boiling components, which penetrate through the bottom of the extraction column. A small volume of the total condensate, which is obtained at the top, is intentionally "blown out" or recirculated into the first column for such trace amounts of minor contaminants to be finally taken to the top of the system and out.

With the second column operating as a pressure column, part of the vapor being collected at the top may be used to provide heat to the first distillation column. However, at higher pressures, the difference between relative volatilities for the respective components is lower, therefore, for same product purities and same heat loads in the evaporator, the pressure column needs more trays.

In a three-column methanol rectification system, the third column is designed to separate methanol from ethanol. One of the methods to remove ethanol is by "blowing out" a small stream above the feed tray in the refining column, or by collecting an ethanol-methanol mixture at the top of the refining column, followed by separation of the two components in the third column. The feed to that column contains nearly all of the ethanol present in the feedstock (crude methanol) plus the methanol product. Water and trace amounts of higher alcohols are removed from the column together with ethanol while pure methanol is collected overhead. The pasteurization section is located above the product collection point.

4. Production of gasoline

Gasoline is a hydrocarbon mixture of roughly 100 of various compounds, obtained by the straight-run and destructive processing of petroleum. The fractions, found in gasoline, include the paraffin fraction (40...65)% (V/V), naphthene fraction (20...35)% (V/V) and aromatic fraction: (8...20)% (V/V).

Taking into account the desirable method of combustion, gasoline should preferably contain large amounts of aromatic hydrocarbons, obtained mainly by reforming and partly by pyrolysis. Very important components – especially in aviation fuels – are mixtures of hydro-carbons obtained in isomerization and alkylation processes (isoparaffins). Highly resistant to knocking combustion, they have the added advantage of a sufficiently high calorific value.

All the components that are required for gasoline blending are obtained in the respective types of refining processes and are combined in the blending unit in accordance with process requirements for the specific gasoline types. Major components of gasoline are listed in Table 1. The respective components are blended so as to obtain a final product (commercial gasoline) which complies with the requirements of applicable standards.

Most of those qualitative parameters of fuels are only approximate because their fractional and chemical composition is very complex. Numerical values for the respective qualitative parameters are selected in a manner which, in as far as possible, enables compliance with

performance requirements, resulting from the design and mode of operation of spontaneous-ignition engines fuelled by such blends.

Component	Boiling point/range [°C]	RON	Function or use
Base cut from distillation	45 ÷ 195	40 ÷ 54	Essential component of gasoline
Butane	0	95	Facilitates cold engine start, component of automotive gasoline
Pentane-hexane fraction	27 ÷ 65	45 ÷ 93	Enables continuous combustion during startup, when present in automotive and aviation gasoline types
Light distillate	65 ÷ 90	-	same as above
Reforming product: - complete	-	-	Major component of automotive and aviation gasoline types, resistant to detonation combustion
- de-aromatized	45 ÷ 200	92 ÷ 101	
- de-xylenated	-	-	
- refined reformate	-	-	
Hydrocracking fraction	40 ÷ 200	72 ÷ 85	Component of automotive and aviation gasoline types with good anti-detonation properties and low sulfur content
Catalytic cracking fractions	40 - 200	91 – 93	Widely used as a component of high-octane gasoline
Hydrogenated pyrolysis gasoline	60 ÷ 200	96 ÷ 99	Used in smaller amounts, especially for automotive gasoline
Polymerization gasoline	60 ÷ 200	94 ÷ 96	Less important, high-octane component of gasoline
Isooctane (2,2,4-trimethylpentane)	111	100	High-octane component of aviation fuels
Various alkylates	40 ÷ 150	93 ÷ 96	Widely used in blends of aviation gasoline (usually), and automotive gasoline (less frequently)
Various isomerisates	40 ÷ 70	82 ÷ 85	Desirable as components of gasoline types for high-duty applications
Additives	-	-	Component which improves lubrication and resistance to detonation combustion, depending on its essential composition

Table 1. Characteristics of gasoline components

The quality or properties of fuels affect a number of processes, connected with their use in a wide sense. The impact of the most significant qualitative parameters of fuels for spark-ignition engines on the various performance processes has been established in a number of tests. The criteria are shown in Table 2.

Requirements relating to gasoline			
Storage, distribution, fuelling	Formation of fuel-air mixture	Optimum combustion	Environmental impact
Density	Chemical composition	Chemical composition	Formation of toxic components of emissions
Chemical stability	Fractional composition	Fractional composition	
Corrosive effect	Vapor pressure	Calorific value	
Level of contamination	Heat of evaporation		
Low-temperature properties	Washing properties	Resistance to detonation combustion	Biodegradability
Electrostatic properties	Density		
Fire safety	Viscosity		

Table 2. Qualitative criteria of gasoline in their performance processes

5. Obtaining of diesel fuels

Diesel fuels are made by blending fractions having boiling ranges from 190°C to 350°C, obtained from petroleum processing in the following technologies:

- an oil fraction from atmospheric distillation (base fraction) of which the properties depend on the chemical nature of petroleum;

- an oil component obtained by thermal cracking; it has a low cetane number, low stability, and a considerable content of unsaturated hydrocarbons;

- an oil component obtained by catalytic cracking, which has a rather low cetane number (CN=40…60) because of a content of aromatic hydrocarbons;

- an oil component obtained by hydrocracking, used for reducing the corrosive effect of diesel fuels by decomposing sulfur compounds in the process; the amount of the hydrocracking product component which is present in the finished diesel fuel determines the oil category in respect of its content of sulfur links;

- an oil component obtained by dewaxing; it deteriorates spontaneous-ignition properties of oils while much improving their low-temperature properties;

- a light oil fraction obtained by vacuum distillation (depending on the grade of petroleum being processed) which increases the amount of oil product thus reducing its volatility and increasing its viscosity and density.

- Depending on the intended use, diesel fuels are blended essentially in two groups:

- diesel fuels for high-speed engines;

- diesel fuels for medium-and low-speed engines; another type of blends comprises so-called heating oils which are intended for use in steam boilers for marine or land applications, industrial furnaces (in rolling mills, glass works etc.), firing up coal dust-fired steam boilers, and for technological reasons.

- The following improvers can be added to diesel fuels, depending on their intended application:

- pro-detonators – to increase the cetane number of diesel fuels;

- corrosion inhibitors – to reduce the corrosive effect of diesel fuels and their combustion products;

- oxidation inhibitors – to improve diesel fuels in terms of stability, enable longer storage;

- depressants – to lower the freezing point of diesel fuels;

- additives which reduce the smoke level in exhaust gases by improving the combustion process.

Those fuels for spontaneous-ignition engines (diesel fuels) which have the desirable composition are expected to show the following characteristics:

- ensure the correct functioning of the fuel system, especially the injection assembly;

- ensure a correct and energy-efficient combustion;

- ensure reduction of toxic components and solid emissions;

- guarantee chemical stability in the storage process.

The qualitative criteria for diesel fuels which are important for the whole area of their application are shown in Table 3.

	Requirements relating to diesel fuels			
	Storage and distribution	Functioning of fuel distribution system	Atomization, evaporation, and combustion	Environmental impact
Properties of fuels	Density	Density	Viscosity	Formation of toxic components of emissions
	Chemical stability	Viscosity	Surface tension	
	Low-temperature properties	Low-temperature properties	Spontaneous ignition properties	
	Corrosive effect	Lubrication	Spontaneous ignition properties	
	Resistance to microbial contamination			
	Electrostatic properties	Level of solid contaminants and water	Calorific value	Biodegradability
	Foaming			
	Fire safety.		Washing properties	

Table 3. Qualitative criteria of diesel fuels in their performance processes

Regardless of standard fuels, for which applicable standards and approved testing methodologies exist, a number of alternative fuels are known, including biofuels, which can be applied as propulsion materials. Such fuels are used in typical spontaneous-combustion engines, of which the designs are adapted to the properties of conventional (standard) fuels. Therefore,

taking into consideration engine requirements, the scope of the respective evaluation criteria ought to correspond to those which apply to conventional fuels. Existing alternative fuels for spontaneous-combustion engines for various applications are listed in Table 4.

Alternative fuels for use in engines			
Form	**For spark-ignition engines**	**For spontaneous-ignition engines**	**For stationary engines**
Liquid		methanol	
		ethanol	
		butanol	
	other alcohols (*tert*-butyl TBA, *sec*-butyl SBA, isopropyl IPA, neopentyl-NPA);	fatty acid esters (FAME, FAEE) from transesterification of rapeseed, soy, sunflower oils	
	ethers (ethyl-*tert*-amyl TAEE, ethyl-*tert*-butyl ETBE, methyl-*tert*-amyl TAME, methyl-*tert*-butyl MTBE, diisopropyl DIPE);		tall fuels (TPO-tall pitch oils) obtained by esterification with ethyl / methyl alcohols of tall oils obtained from gums/resins of coniferous trees (side products in sulfate cellulose production processes and low-temperature dry distillation of wood);
	hydrogen-based synthetic fuels (including BG, FT, HTU processes)		
	liquefied petroleum gas (LPG)		
	dimethylofuran (DMF)	fuel-water emulsions (aquasols)	
		pure vegetable oils	
Gaseous	liquefied natural gas (LNG)		
	compressed natural gas (CNG)		
	biomethane from biogas		biogas
	dimethyl ether (DME) and (contemplated) diethyl ether (DEE);		
	gaseous fuels from CtG processes		
	hydrogen		

Table 4. Alternative fuels for use in engines

In view of the above data, for a rational assessment of the quality of fuels and their usefulness, especially after storage processes, in engine operation it is necessary to chose applicable assessment criteria and methodology, enabling a relatively fast analysis of changes in the parameter values. The choice of such criteria ought to result from the sensitivity of the respective criteria to fuels' oxidation and contamination, potentially causing the accepted and recognized limiting values to be exceeded both in respect of their measure and weight.

Experience in using engine fuels indicates that their quality may change, mainly in storage and distribution processes. This causes the necessity to establish the scope and frequency of the quality surveillance of fuels. Some of the generally adopted types, scopes, and frequencies of control of the quality of fuels in their distribution chain are shown in Table 5.

Fuel type and scope of control	Fuel distribution step
Full – comprising assessment of the values of all quality parameters of fuels, as described in the standard ON-EN 228 for gasoline and PN-EN 590 for diesel fuels	• Refinery – before delivering a fuel lot for distribution; • Storage facilities – after acceptance of fuel for storage and on its release, or periodically, every 6 months of storage
Control – comprising assessment of selected parameters, usually appearance, density, fractional composition, and vapor pressure – for gasoline, or flash point and cold filter plugging point – for diesel fuels.	• Storage facilities – periodically, during storage; • Fuel station – random analysis, for instance every 3 to 4 deliveries, after acceptance of fuel for storage.
Short – comprising determination of density, fractional composition, content of water and contaminants – for diesel fuels, or appearance, color, density – for gasoline.	• Fuel station – before acceptance of fuel for storage; • Storage facilities – before unloading tankers.

Table 5. Fuel types and scopes of analysis in the distribution chain

6. Conclusion

The growing demand on liquid fuels necessitates maximization of production output, especially those fuel components which originate from destructive processing. Even though in straight-run processing of petroleum, processes may be conducted which are intended to expand the limits of fractions of base gasoline, kerosine and diesel fuels fractions, yet the main focus is on secondary processing, providing increased numbers and amounts of components of diesel fuels, also by means of thermal and thermocatalytic processes, in the presence or absence of hydrogen.

Owing to the growing number of spontaneous-ignition engines in Europe, the supply of diesel fuels is insufficient while that of gasoline is excessive. As a result, technological processes are carried out which provide the maximum yield of propellant cuts and the residues are processed to provide components which are useful for diesel fuel blending processes.

Experiments were made in which fractions resulting from depolymerization of plastics (KTSF fraction) were "sunk" in petroleum or components which result from re-refining of spent lubricating oils were utilized.

In the production of gasoline, if correct process conditions are maintained, components obtained in isomerization processes, catalytic reforming, full hydrocracking, alkylation (using isobutane) and fluidized-bed cracking (FBCC) are not expected to affect the stability of gasoline during long-term storage.

As regards the motors spirits manufacturing and blending technologies, the following fractions, which originate from the processes of technology discussed above, may very much reduce the duration of safe storage of such fuels:

- the gasoline fraction obtained by thermal cracking of the vacuum column residue, which was not hydrogenated;

- alternately, the non-hydrogenated fraction of pyrolysis gasoline;

- fractions from synthesis of gaseous hydrocarbons;

- ethanol as a biocomponent.

The contemporary diesel fuel blending techniques are typically based on the combining of components derived from the following major process unit:

- distillation in a tube-tower distillation system

- hydrocracking;

- fluidized-bed cracking (FBCC);

- hydrodesulfurization of soft asphalt;

- thermal processing of residue.

The stability of diesel fuels can be much affected by the following factors:

- components from thermal processes;

- biocomponents (FAAE);

- components from WtL processes (KTSF fraction) and re-refining products of the processing of spent lubricant oils.

Some refineries offer co-hydrogenation of petroleum fractions and vegetable oils. The solution carries a potential risk to the blend stability because the process mechanism, connected with the presence in such oils of heterogenic compounds, is not very well known.

Generally, the stability of fuel blends is the lower, the more unsaturated bonds such as those in alkenes (or olefins) they contain.

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