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Improvement of Operational Properties of Technological Fuel - A Review

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Abstract

An overview of the ways of improving the operational properties of furnace and boiler fuels has been presented; their positive and negative features have been analyzed. It has been established that the most effective way to improve the operational properties of furnace and boiler fuels is their compounding with additives as well as various components since it is easy to implement under conditions of direct application of process fuel. It has been suggested that a very successful alternative to the additives and components used in industry can be fractions (components) obtained by thermal destruction in the temperature range of 300-380°C of secondary polymer raw materials, represented by polyethylene, polypropylene, and polystyrene.

Keywords*: Technological fuel; Secondary raw materials; Polyolefins; Thermal destruction; Quality indicators; Operational properties.*

1. Introduction

The main types of process fuels are furnace and boiler fuels, which today are in wide demand in the implementation of many technological production processes. These fuels are used to generate heat energy in various power plants and industrial furnaces. Considering the current environmental and economic trends prevailing in the EU countries, it should be noted that improving the operational properties of technological fuel is a priority task, which is especially urgent for major producers occupying a leading position in the energy market.

2. Research objective

Among the operational properties of the process fuel to be improved, the following can be distinguished: ensuring the completeness of fuel combustion, minimizing harmful emissions, increasing the heat of combustion, reducing energy costs associated with heating and pumping fuel through pipelines. All this can be achieved both in the production of process fuel and in its direct application (see Fig. 1).

In accordance with the information given above, the purpose of this work is a detailed analysis of each method shown in Fig. 1. as well as the choice of the most optimal of them, allowing to achieve a significant effect with minimal material costs.

The layout of the process flow diagram, the materials of the main technological devices, the list of necessary measures to protect the environment and, of course, the operational properties of the products obtained, expressed in terms of certain quality indicators, largely depend on the quality of the processed raw materials. However, it should be noted that the world oil refining industry is forced to develop in an era of acute shortage of quality raw materials [1].

And this, in turn, necessitates expanding the raw material base and improving the existing process for the production of technological fuel.

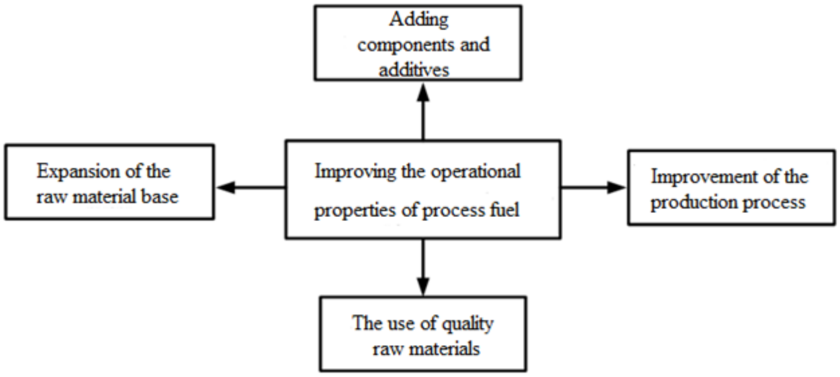

Figure 1. Block diagram showing the ways to improve the operational properties of process fuel

The main reason for the search for an alternative source of raw materials for the implementation of the technological process of fuel production is both to ensure the uninterrupted operation of the installations and to reduce the cost of the products. At the same time, in the last decade, there has been an active involvement in the technological process of secondary energy resources, which are mainly represented by various industrial and household waste [2-3]. The most demanded of them are waste oil products, oil sludge, and used car tires.

Thus, there is a known technology for processing waste lubricating oils by means of low-temperature pyrolysis at a temperature of 450-550°C, which makes it possible to obtain a pyrolysis gas, a liquid product with properties reminiscent of diesel oil (up to 85% of the initial raw material) and a pyrolyzed residue, which is a product similar to technical carbon. At the same time, the liquid product can be used as a boiler or heating oil [4-6]. Similar technology is used to process oil sludge and used car tires, but with certain features of the process.

Oil sludge is pyrolyzed at an average temperature of 300–450°C, less often up to 500°C to form a liquid product that has similar qualities and properties with low-grade petroleum distillates of oil refineries and can be used as a process fuel for power plants. By-products are pyrolysis gas and solid carbonaceous residue [7-10].

As for the used car tires, their pyrolysis includes heating the raw material to temperatures> 400°C without access to oxygen to obtain a liquid fraction, gas, and semi-coke. The liquid fraction obtained as a result of pyrolysis can be used directly as a process fuel, fuel components, or for the production of chemicals. Gases usually consist of hydrocarbons C1-C4 and hydrogen, so they can serve as fuel for the pyrolysis process. Solid semi-coke, as a rule, consists of particles of a metal cord and carbonaceous residue [11-12].

It should be noted that the technology of pyrolysis of waste lubricating oils, oil sludge, and used car tires has not found its industrial distribution due to high production costs associated with the specific composition of raw materials. So, waste oils have a fairly high cost compared to other secondary raw materials, and for the most part, they undergo regeneration and reuse for their intended purpose.

Oil sludge contains a significant amount of water, acidic components, and mechanical impurities (40-80% of the raw material), which ultimately complicates its processing and significantly increases the cost of this process.

Recycling of used car tires is hampered by the presence of a metal cord in them, which is quite problematic to extract. In addition, it becomes necessary to conduct the process in the absence of air using rotating retort furnaces, and the resulting liquid product (pyrolysis liquid) contains in its composition a significant amount of unsaturated hydrocarbons, which cause resinification and a characteristic strong smell of the obtained liquid product. In this case, the solid product - semi-coke is characterized by the increased ash content due to the presence of metal cord particles in it.

As to such a method as improving the production process, it is the most energy-intensive since it is mainly associated with the re-equipment of the existing production (changing the design of the apparatus, the use of new structural materials, the design of purification systems and the neutralization of harmful emissions). Therefore, at the moment, it can be viewed as a somewhat distant prospect.

The addition of components and additives to the process fuel to improve its operational properties, in comparison with all the approaches described above, is the most cost-effective and, due to its simplicity, can be implemented in places where the process fuel is directly used [13-14]. The introduction of additives into the process fuel helps to stabilize the fuel combustion process, reduce the number of deposits in combustion chambers, reduce wear-out and corrosion of technological equipment, and improve viscosity-temperature and other operational characteristics.

So, to neutralize harmful combustion products, improve combustion efficiency and save process fuel in [15-19], it was proposed to use nanoparticles of metals, oxides, carbides, nitrides, or carbon nanotubes. The neutralization of harmful combustion products is carried out due to the chemical binding of SO_2 and SO_3, with the formation of neutral compounds that do not cause corrosion of equipment. Also, a certain inhibition of the oxidation process of SO_2 to SO_3 or the reduction of SO_2 to SO_3 can be observed directly in the fuel combustion zone.

An increase in the efficiency of combustion of process fuel is achieved due to the peptizing effect of the additive, which contributes to a more uniform distribution of easily and hardly combustible parts in a drop of process fuel, and an increase in the completeness of the reaction of substances in the combustion reaction, which leads to complete combustion of fuel and a decrease in soot formation. In terms of efficiency, metals, as combustion catalysts, are arranged in the following order: Mn > Sn > Cu > Co > Zn > Mo > Mg > Fe > Ca [20].

Known multifunctional additive, developed by ERC, it is able to improve the environmental properties of process fuel [21].

In work [22], it was proposed to use Diproxamine-157, which, in addition to the destruction of emulsions of process fuel with water, is also capable of being adsorbed on the surface of nascent crystals of paraffinic hydrocarbons and prevents their growth and association, thereby reducing the viscosity and pour point of the fuel. This, in turn, helps to reduce energy costs for fuel heating and to pump through pipelines.

An industrial polymer additive 19% ethylene-vinyl acetate copolymer can be used as an additive to process fuel, which at a concentration of 300 ppm lowers the fuel pour point by 9°C [23].

Of special interest is the formation of the properties of technological fuel by compounding it with various components. Compounding usually occurs according to the principle of adding components with low viscosity to the residues (atmospheric / vacuum processing or thermal cracking) from the distillation of high-viscosity crude oil in proportions necessary to meet the requirements of regulatory and technical documentation for fuel [24].

It should be noted that all the additives described above have a number of significant drawbacks that limit their industrial use, which includes:

- a high cost;
- a complexity of obtaining;
- a low efficiency;
- the necessity to use special systems for dosed injection and dispersion in the volume of fuel (especially for solid additives);
- the usage of components that are widely used in other processes for the production of petroleum products.

All these drawbacks cause the fact that the question of finding effective and relatively inexpensive components that make it possible to obtain high-quality technological fuel is still open.

3. Results and discussions

Considering all of the above, it can be assumed that an alternative to existing industrial additives and components are products obtained by thermal destruction of secondary polymer raw materials, for example, polyolefins: high and low-pressure polyethylene, polypropylene, and polystyrene. Using secondary raw materials, on the one hand, will significantly reduce the cost of the products obtained; on the other, it improves the global environmental situation.

A positive feature of polyolefins makes it possible to carry out their technological processing, and it is also their ability to undergo thermal degradation at relatively low temperatures of 300-380°C with the formation of products with a lower molecular weight than the feedstock (monomers and different lengths of fragments of the hydrocarbon chain).

The mechanism of thermal destruction was considered in the works [25-27] and consists of the following stages: initiation, chain decay, chain transfer, and chain termination.
The initiation consists of breaking the C-C bond and the formation of free radicals

$$\sim CH_2\text{-}CH_2\text{-}CH_2 \,\vdots\, CH_2\text{-}CH_2\text{-}CH_2\sim \xrightarrow{t,{}^{\circ}C} \sim CH_2\text{-}CH_2\text{-}H_2C^{\cdot} + {}^{\cdot}CH_2\text{-}CH_2\text{-}CH_2\sim \tag{1}$$

Chain decomposition ends with the formation of a monomer at the free radical ends of the chains

$$\sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2 \,\vdots\, CH_2\text{-}CH_2^{\cdot} \longrightarrow \sim CH_2\text{-}CH_2\text{-}CH_2\text{-}H_2C^{\cdot} + CH_2{=}CH_2 \tag{2}$$

The chain transfer stage can be characterized by the abstraction of a hydrogen atom of another chain by a free radical or the abstraction of a hydrogen atom from its own chain. This forms a new free radical, a saturated and unsaturated group

$$\begin{gathered}\sim CH_2\text{-}H_2C^{\cdot} + \sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2 \,\vdots\, CH_2\sim \longrightarrow \\ \longrightarrow {}^{\cdot}CH_2\sim + \sim CH_2\text{-}CH_3 + \sim CH_2\text{-}CH_2\text{-}CH{=}CH_2\end{gathered} \tag{3}$$

The final stage is a chain termination with the resulting recombination of two free radicals; it ends with the formation of a new polymer chain. In this case, the products of thermal degradation of polyethylene and polypropylene are mainly represented by chain fragments of various lengths and a small amount of monomer [25-26].

And this, in turn, is a positive moment when using thermal destruction to obtain a product that will not consist of a monomer (gas), but of these fragments of a polyethylene or polypropylene chain, and which by its properties can be used as a component of a technological fuel.

Thermal degradation products of polystyrene consist of a monomer, a dimer, and a trimmer. These compounds are detached from the polymer chain with free radicals at the ends. In some cases, the formation of fragments of the polymer chain with one saturated and one unsaturated end of the chain occurs in connection with the transfer of a hydrogen atom.

So, the reactions of thermal destruction of polystyrene can proceed according to the following mechanism [25-27].

Here is decay without hydrogen transfer

$$\begin{gathered}\sim CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_2 \,\vdots\, CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_2\sim \longrightarrow \\ \longrightarrow \sim CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}H_2C^{\cdot} + {}^{\cdot}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_2\sim\end{gathered} \tag{4}$$

Any of the free radicals are capable of splitting off an intramolecular or intermolecular hydrogen atom, and it can cause a new decomposition in the polymer chain (free radical transfer) [25,27]

$$\begin{gathered}\sim CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}H_2C^{\cdot} + \\ + \sim CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5) \,\vdots\, CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_2\sim \longrightarrow \\ \longrightarrow \sim CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_3 + \sim CH(C_6H_5)\text{-}CH_2\text{-}{}^{\cdot}CH(C_6H_5) + \\ + CH_2{=}C(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_2\sim\end{gathered} \tag{5}$$

In some cases, chain decomposition with the formation of a monomer can be observed

$$\sim CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}H_2C^{\cdot} \longrightarrow \\ \longrightarrow \sim CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}H_2C^{\cdot} + CH(C_6H_5){=}CH_2 \quad (6)$$

Here is decay accompanied by hydrogen transfer

$$\sim CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_2\sim \longrightarrow \\ \longrightarrow \sim CH_2\text{-}CH(C_6H_5)\text{-}CH_2\text{-}CH_2(C_6H_5)\sim + \\ + CH_2{=}C(C_6H_5)\text{-}CH_2\text{-}CH(C_6H_5)\text{-}CH_2\sim \quad (7)$$

The products of thermal destruction of polymer raw materials can be considered as a wide fraction, which, when fractionated, is crushed into narrower fractions shown in Fig. 2.

It should also be noted that, depending on the parameters of thermal degradation (pressure, heating rate of raw materials, and final degradation temperature), the resulting fractions may not include fraction IV, which is similar in properties to wax and can be used in the production of greases. That is, the more severe the conditions for the occurrence of thermal destruction are, the lower the molecular weight of the resulting products is, as well as the final boiling point of the wide fraction.

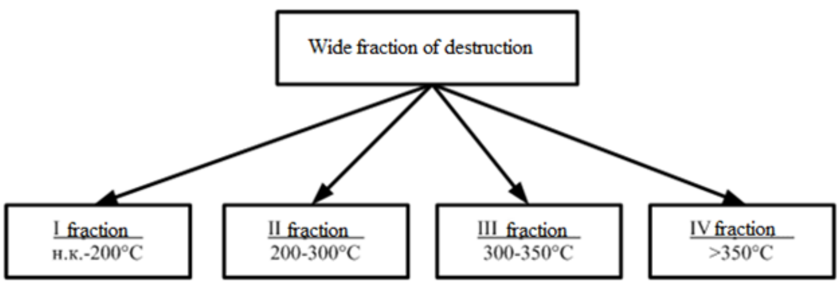

Figure .2 Products obtained by fractionation of a wide fraction thermal destruction

Depending on the technological necessity, the temperature limits of the obtained fractions can change, which is associated with the variation in the values of such indicators of the technological fuel as the heat of combustion, viscosity, flash point, and pour point.

The scheme for obtaining process fuel is shown in Figure 3. It can be implemented in the conditions of oil refining enterprises and consisting of sequential technological stages.

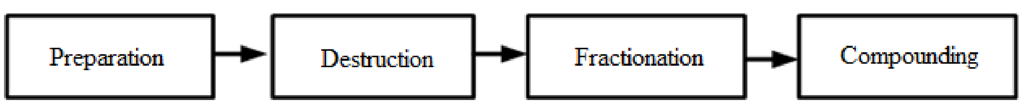

Figure 3. Block diagram of production of process fuel using components obtained from secondary polymer raw materials

According to this scheme, at the stage of preparation, washing, drying, and rough (up to 20×10^{-2} m) crushing of polymer raw materials occur, and it makes it possible to intensify the next stages of the process and reduce the overall dimensions of the technological equipment. Further, the stage of destruction of the prepared raw material takes place in a reactor-type apparatus at atmospheric or elevated pressure. After that, the products pass the stage of fractionation in a packed-type apparatus, where, depending on the temperature of the beginning and end of boiling, the necessary fractions are isolated. The final stage of the technological process for the production of technological fuel is the compounding of the obtained fractions (components) with hydrocarbon fractions obtained from petroleum feedstock to obtain the final product that meets the requirements of regulatory and technical documentation.

4. Conclusions

Based on the analysis of the data given in the technical literature, we note that the most effective way of the existing ones to improve the operational properties of furnace and boiler fuels today is their compounding with additives and various components. This approach does not require technological re-equipment of the existing production and is easily implemented in the conditions of direct application of technological fuel.

It has been suggested that fractions (components) obtained by thermal destruction of secondary polyolefin raw materials can act as a very successful alternative to the additives and components used in the industry.

By varying the technological parameters of destruction and the temperature limits of the boil-off of fractions, it is possible to obtain technological fuels with the required value of the heat of combustion, viscosity, flash point, and solidification point, on which the energy efficiency, fire and explosion hazard of production as a whole depend. The flash point, along with the content of water and mechanical impurities, can become a criterion in the selection and determination of the required depth of preparation of one or another raw material for use as a dispersion medium in the production of greases.

References

[1] Demina OV. Global hydrocarbon markets: effective strategies of players. Spatial Economics. 2018; 3: 67-87.
[2] Egorov AN, Egorova GI. Waste from petrochemical industries - raw materials for resource-saving technologies. TIU, 2016; p. 190.
[3] Beltramini JN, Lu GQ. Processing of Primary and Secondary Fuels: Perspective on Petroleum Refining. Energy Storage Systems. 2001; 2: 619-634.
[4] Kurmaev RN, Glushankova IS, Weisman YaI. Selection and substantiation of the method of utilization of waste oils at large industrial enterprises. Transport. Transport facilities. Ecology. 2016; 1: 38-51.
[5] Chernomurov FM. Energy and resource saving in the oil and gas chemical complex: textbook. Yekaterinburg, 2014: p. 236.
[6] Kozhevnikov VA. The potential for the use of waste oils for the needs of heat supply. Electronic magazine of the energy service company "Ecological systems". 2008; 8. – URL: http://journal.esco.co.ua/2008_8/art038.htm.
[7] Shen L, Zhang DK. An experimental study of oil recovery from sewage sludge by low-temperature pyrolysis in a fluidized. Fuel. 2003; 82: 465–472.
[8] Schmidt H, Kaminsky W. Pyrolysis of oily sludge in a fluidised bed reactor. Chemosphere. 2001; 45: 285–290.
[9] Chang CY, Shie JL, Lin JP, Wu CH, Lee DJ, Chang CF. Major products obtained from the pyrolysis of oily sludge. Energ Fuel. 2000; 14 :1176–1183.
[10] Wang Z, Guo Q, Liu X, Cao C. Low temperature pyrolysis characteristics of oily sludge under various heating conditions. Energ Fuel. 2007; 21: 957–962.
[11] Martínez JD, Puy N, Murillo R, García T, Navarro MV, Mastral AM. Waste tire pyrolysis – a review. Renew Sust Energ Rev. 2013; 23: 179–213.
[12] Williams PT. Pyrolysis of waste tyres: a review. Waste Manag. 2013; 33(8):1714–28.
[13] Zvereva ER. Resource and energy saving technologies in fuel oil farms of thermal power plants. Kazan: Kazan. state energ. un-t, 2010; p. 184.
[14] Danilov AM. Improving the combustion efficiency of boiler fuels using the VNIINP-200 additive. Industrial energy. 1996; 8: 12–13.
[15] Basha SJ, Anand RB. Role of nanoadditive blended biodiesel emulsion fuel on the working characteristics of a diesel engine. J. Renewable Sustainable Energy. 2011; 3: № 023106.
[16] Basha SJ, Anand RB. Experimental Investigations on the Effects of Cerium Oxide Nanoparticle Fuel Additives on Biodiesel. Journal of the Brazilian Society of Mechanical Sciences and Engineering. 2013; 35 (3): 257–264.
[17] Sajith V, Sobhan CB, Peterson GP. Experimental Investigations on the Effects of Cerium Oxide Nanoparticle Fuel Additives on Biodiesel. Advances in Mechanical Engineering. 2010; 2010: № 581407.
[18] Jung HS, Miller A, Park K, Kittelson DB. Carbon nanotubes among diesel exhaust particles: real samples or contaminants? 2013; 63 (10): 1199–1204.

[19] Tewari P, Doijode E, Banapurmath NR, Yaliwal VS. Experimental Investigations on a Diesel Engine Fuelled with Multiwalled Carbon Nanotubes Blended Biodiesel fuels. International Journal of Emerging Technology and Advanced Engineering. 2013; 3: 72–76.
[20] Zvereva ER. Fuel oil additives. Energy problems. 2011; 1-2: 7-17.
[21] Mueller M. Performance additives for modern heating oil’s; Performance-Additiverung moderner Brennstoffe. Germany. Erdoel Erdgas Kohle. 2010; 126: 86-90.
[22] Zvereva ER, Mingaleeva GR, Khabibullina RV. Improvement in the viscosity characteristics of boiler oil by additives. Pet. Chem. 2016; 56: 65–67.
[23] Farazmand S, Ehsani MR, Shadman MM, Ahmadi S, Veisi S, Abdi E. The effects of additives on the reduction of the pour point of diesel fuel and fuel oil. Journal Petroleum Science and Technology. 2016; 34(17-18): 1542-1549.
[24] Iarc monographs on the evaluation of carcinogenic risks to humans. Occupational Exposures in Petroleum Refining; Crude on and Major Petroleum Fuels. 1989; 45.
[25] Suberlyak OV, Sembay EI. Fundamentals of polymer chemistry: textbook, 2005; p. 240.
[26] Suberlyak OV, Skorokhoda VI, Semenyuk NB. Theoretical foundations of chemistry and technology of polymers: textbook. Lviv: Lviv Polytechnic Publishing House, 2014; p. 336.
[27] Zakharchenko MI, Seredenko VV, Taranenko IM. Chemistry of polymers: textbook. Nat. aerospace University «Khark. aviation. Inst», 2008; p. 234.

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