

JANUSZ MAGIERA\*, MIECZYŚLAW MARKIEWICZ\*\*,  
ANETA GŁUSZEK\*\*\*

## HYDROFINISHING OF DISTILLATES OBTAINED FROM WASTE OILS (WOs)

The process of hydrofinishing of waste oils (WOs) after high-vacuum distillation has been analyzed; the process leads to a reduction of organic compounds containing nitrogen, hydrogen, sulphur, and metals. Based on the example of product balance the improvement of crucial performance parameters of oil bases after hydrofinishing (hydrotreatment) has been shown. A substantial reduction has also been proved in the amount of sulphur emitted along with exhaust gases (fumes) from diesel engines (compression-ignition engines) which use hydrofinished diesel oil for combustion purposes.

### 1. INTRODUCTION

Transport and industry use large volumes of lubricating oils which afterwards become waste oils (WOs). In many countries, Poland [1] included, WO are considered hazardous waste materials as they contain a number of harmful and even carcinogenic substances such as products of oxidation and thermal decomposition of hydrocarbons (PAH) and/or PCB, compounds of sulphur, phosphorus, chlorine and nitrogen blended into oils as additives (detergents, viscosity modifiers, corrosion inhibitors), metals (including: Ca, Zn, Mg, Cd, Pb, Ni, V) and other foreign matter [2]. About 300,000 tonnes of lubricating oils enter the Polish market annually, a part of which defined as a collection potential [3] should be selectivity collected and regenerated. The necessity of collection and management (utilization) of WO is fully justified by the potential risk (hazard) they pose to soil, air and underground waters in case such oils should be accidentally released to the environment in an uncontrolled way. It is estimated that 1 kg of WO may poison 5 million litres of potable water [4], and if WO is burnt in an im-

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\* Institute of Chemical Engineering and Physical Chemistry, Cracow University of Technology.

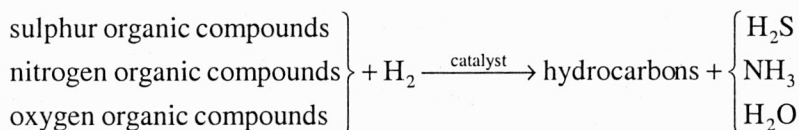
\*\* Jedlicze Petroleum Refinery, Joint Stock Company.

\*\*\* Cracow University of Technology.

proper way it causes the emission of heavy metal oxides, dioxins and furans. Besides, WOs form alternative raw material (feedstock), valuable for economic reasons, 600–700 kg of secondary (recycled) lubricating oils may be obtained, through regeneration, from 1000 kg of WO, while only 150 kg of virgin oils [5] are produced from one tonne (MT) of crude oil. However, the processing of such feedstock as WO should be carried out according to the rules of ecology, i.e., in an energy efficient way and possibly preventing the environment from pollution. The contemporary refining and petrochemical industry strives for the development of re-refining processes – for the production of fuels, base oils, lubricants (greases) and derivative products, more environmentally friendly, i.e., of possibly lowest content of sulphur, lead, polynuclear aromatic hydrocarbons, heavy metals and other harmful components, the processes being based on the technologies of hydrorefining or hydrofinishing.

## 2. HYDROFINISHING – DEFINITION, FACTORS AFFECTING THE PROCESS

Hydrofinishing of oil-derived feedstock is a catalytic process in which sulphur, nitrogen, and oxygen, as well as metals [6] are removed from hetero-organic compounds. The basic reactions which take place during hydrofinishing are: hydrodesulphurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrodemetallization (HDM). Hydrocracking and hydrogenation of aromatic rings accompany the removal of heteroatoms and metals. General reactions of hydrofinishing can be illustrated in the following reaction network [6]:



The effectiveness of the hydrofinishing process is determined by the selection of appropriate catalysts and optimal conditions of the reactor operation. The process uses the bimetallic catalysts containing the molybdenum or tungsten ions together with the cobalt and nickel ions deposited (settled) on aluminium oxide, zeolites, aluminosilicates or activated carbon. It is very important to select a right catalyst whose high activity will allow achieving a high degree of conversion in the process conducted. Up to now several models of catalysts for hydrofinishing have been developed, e.g., a mono-layer model, a synergistic model or a Topsøe model connected with the occurrence of the active phase NiMoS or CoMoS [6]. When studying the “dynamics” occurring on the surface of a hydrofinishing catalyst it is possible to distinguish two essential processes:

1. The process connected with the adsorption of an organic sulphur compound and desorption of a hydrocarbon, that is hydrodesulphurization, which may be accompanied by the process of the substrate hydrogenation by means of the hydrogen adsorbed

through dissociation. Then,  $H_2S$  may be split off and the anion vacancy may originate in another place on the catalyst surface.

2. The process of exchange of sulphur atoms connected with the adsorption and desorption of  $H_2S$  and forming the anion vacancy somewhere else.

The following parameters have the essential effect on the quality of the raffinate obtained: the reactor temperature, the partial pressure of hydrogen and the time-length of contact of the load with the catalyst [7], [8]. The reaction pressure is advantageous to the course of all the reactions in the process of hydrodesulphurization. A higher degree of the substrate reaction is achieved and, at the same time, high hydrogen consumption. If the volume of hydrogen is limited, it is necessary to increase the reactor temperature or to decrease the unit capacity (throughput). The longer time of the load remaining in the reactor is more favourable for achieving the required properties of the raffinate but, actually, the main parameter which affects the processes is temperature. It should be high enough to obtain the product of appropriate quality but not too high, in order not to increase the share of undesirable reactions leading to deactivation of the catalyst. It should also be noted that the reactions of hydrodesulphurization are not thermodynamically limited but they depend on the degree of the catalyst deactivation. On the other hand, the reactions of removal of oxygen, sulphur and nitrogen from aromatic rings are thermodynamically limited like the reactions of hydrogenation of aromatic compounds (arenes). The by-reactions of the process are the polymerization reactions which lead to coke formation and hydrocracking reactions due to production of light hydrocarbon cuts, use of hydrogen and lowering the effectiveness of the process.

### 3. THE WASTE OILS RE-REFINING PLANT IN JEDLICZE PETROLEUM REFINERY

Re-refining is a process of regeneration, conducted in specialized plants which make it possible to manufacture base oils through re-refining of waste oils. The amount of the component obtained in the process of regeneration used for blending of lubricating oils cannot, however, be lower than 30% [9]. In technological solutions of WO regeneration, apart from the preliminary stages (pretreatment, water removal, fuel cut removal), the main role is played by single operations such as: vacuum distillation and finishing treatment.

The method of re-refining used at present in Jedlicze Petroleum Refinery is based on the Viscoluble and IFP technological process [10]. Waste oil, pretreated by sedimentation, is mixed with an alkali agent and then preflashed in order to remove water and light hydrocarbon cuts. The dewatered oil, after decanting, is subjected to thermal deasphalting and fractioning distillation. The process of vacuum distillation consists in separating the light phase from the heavy phase which contains metals, resins, tars, asphaltenes, additives and other compounds resulting from decomposition. The

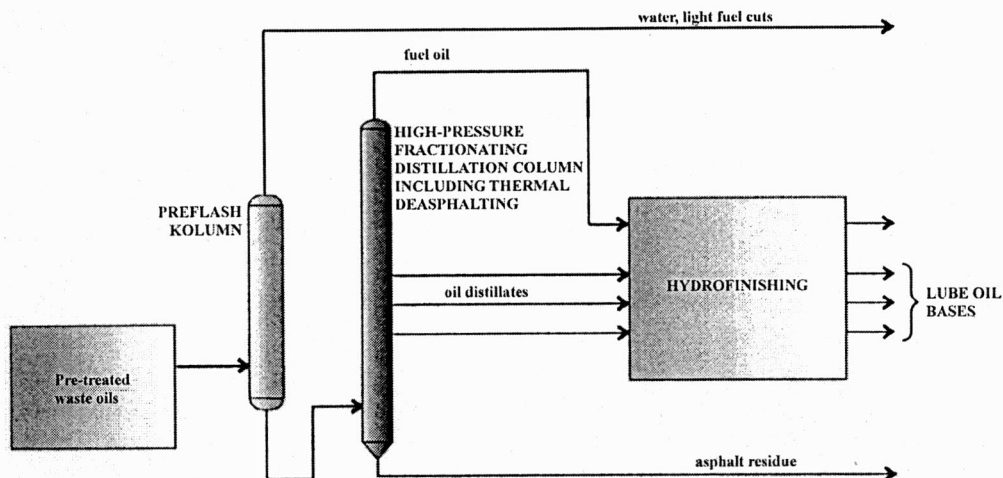


Fig. 1. General flowchart of waste oil re-refining processes in Jedlicze Petroleum Refinery

heavy phase remains at the bottom of the column, while lubricating oils are separated into three side cuts. Only after such treatment the comprehensive hydrofinishing can begin (figure 1). The waste oil hydrofinishing plant is made up of the main hydrofinishing plant (80,000 MT of the distillate a year), the hydrogen producing plant (1000 m<sup>3</sup> of hydrogen an hour), and the plants of amine regeneration, sulphur recovery and sour water stripper.

#### 4. HYDROFINISHING PLANT IN JEDLICZE PETROLEUM REFINERY

Hydrogen of high purity is the feedstock necessary for conducting the hydrofinishing process. The hydrogen is generated in the process of steam-reforming of natural gas. Yet, before the gas is saturated with water, sulphur should be removed from it, since sulphur may cause deactivation of the catalyst in the reformer. The feedstock desulphurization is carried out in a reactor made up of two sections. In the upper part of the unit, there is a bed of the hydrogenation catalyst type CoMo, whereas in the lower part of the unit there is the catalyst with the active zinc oxide, where the reaction of hydrogen sulphide adsorption proceeds (table 1).

The gas after desulphurization is subjected to steam-saturation and then fed to the reformer with the nickel catalyst. There the proper reactions proceed, leading to the generation of hydrogen:

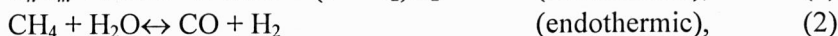
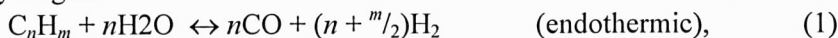


Table 1

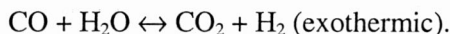
Catalytic reactions of desulphurization of natural gas at 400 °C

Hydrogenation	Adsorption
$R-HS + H_2 \rightarrow R-H + H_2S$	
$R_1-SS-R_2 + 3H_2 \rightarrow R_1-H + R_2-H + 2H_2S$	
$R_1-S-R_2 + 2H_2 \rightarrow R_1-H + R_2-H + H_2S$	$H_2S + ZnO \rightarrow ZnS + H_2O$
$(CH)_4S + 4H_2 \rightarrow C_2H_{10} + H_2S$	
$COS + H_2 \rightarrow CO + H_2S$	

where:

R, R<sub>1</sub>, R<sub>2</sub> are hydrocarbon radicals,(CH)<sub>4</sub>S is thiophene.

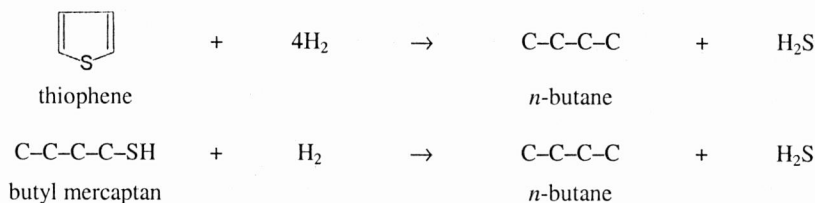
The gas leaving the reformer still contains substantial amounts of carbon monoxide, and that is why it is converted, in the reactor, into CO<sub>2</sub>, producing additional amount of hydrogen:



Distillates of waste oils, after being mixed with fresh compressed hydrogen and the recycle hydrogen, are heated in the process furnace and then they are hydrorefined in two stages. In the first stage, which proceeds on the catalyst bed with highly developed surface, the adsorption of metals and demetallization occur. Even a one-per-million level of contaminants in the form of silicon and metal compounds (mainly those of zinc and lead) is harmful to the catalysts used in hydrotreatment. After passing through the protective bed of the demetallization reactor, the mixture of oil and hydrogen is fed to the hydrofinishing reactor. The hydrogenation proceeds in the presence of the catalysts of molybdenum and nickel oxides set on the porous structure of Al<sub>2</sub>O<sub>3</sub> and, as a result, the volumes of coke and aromatic hydrocarbons are reduced, the termooxidation properties (characteristics) are improved and the colour becomes better. The temperature at the outlet of the reactor depends on the kind of feedstock processed and the phase of the catalyst operation cycle. The average temperature is 300 °C–340 °C, and the reaction pressure is ca. 5.5 MPa.

The typical reactions occurring in the hydrofinishing process are:

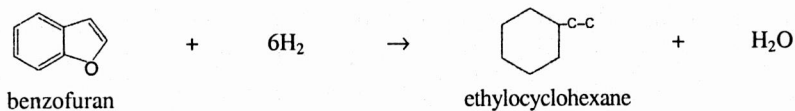
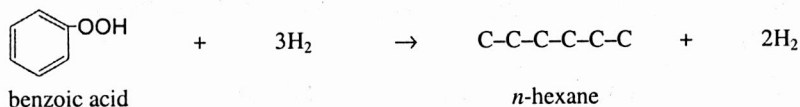
- Removal of organically bound sulphur



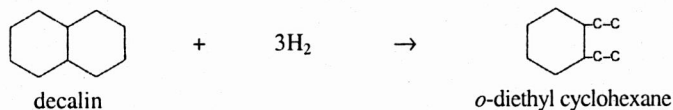
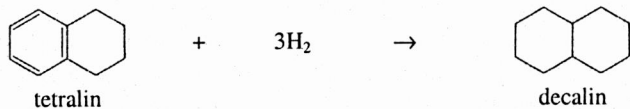
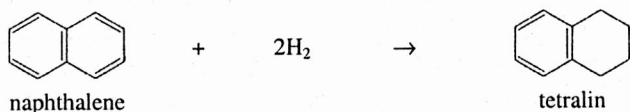
• Removal of nitrogen from organic compounds



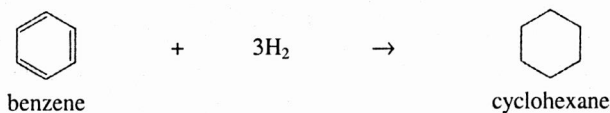
• Removal of organically bound oxygen



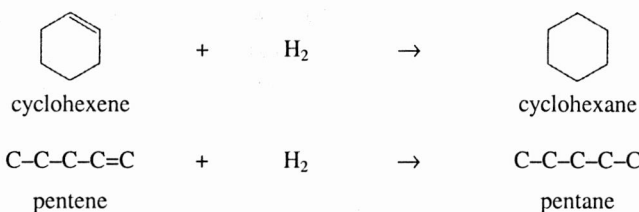
• Removal of sulphur polyaromatic compounds



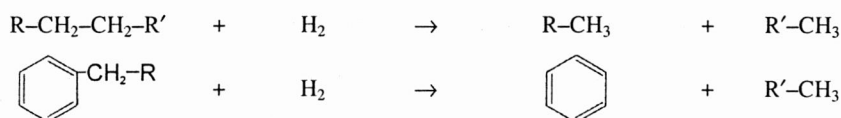
• Removal of sulphur monoaromatic compounds



- Hydrogenation of olefins



- Hydrocracking



- Removal of metals from metal-organic compounds – organic compounds of metals easily decompose and the metals thus formed are adsorbed on the catalyst.

- Polymerization leading to coking.

Examples of mechanisms for selected reactions of HDS, HDN and HDO are presented in figures 2 through 5.

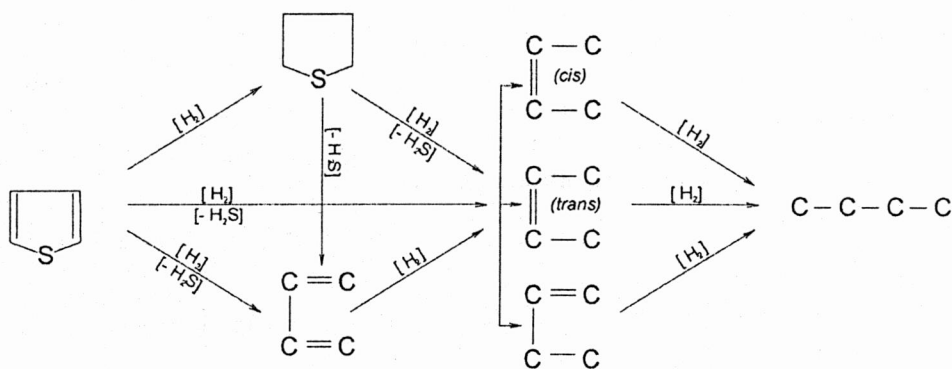


Fig. 2. Reaction pathways proposed for the formation of butane from the HDS of thiophene [11]

The after-reaction mixture goes to the hot high-pressure separator where it is separated into liquid and gaseous phases. The gaseous phase, containing mainly  $\text{H}_2$ ,  $\text{H}_2\text{S}$  and  $\text{CH}_4$ , after being mixed with scrubbing water and hydrogen scrubbing liquid, enters the column purifying the recycle gas. The gas from the scrubbing column is then subjected to the high-pressure amine scrubbing with the use of diethanolamine in order to reduce the concentration of  $\text{H}_2\text{S}$  in it. The purified hydrogen is recycled to the process. The diethanolamine stream, rich in hydrogen sulfide, is directed to the amine

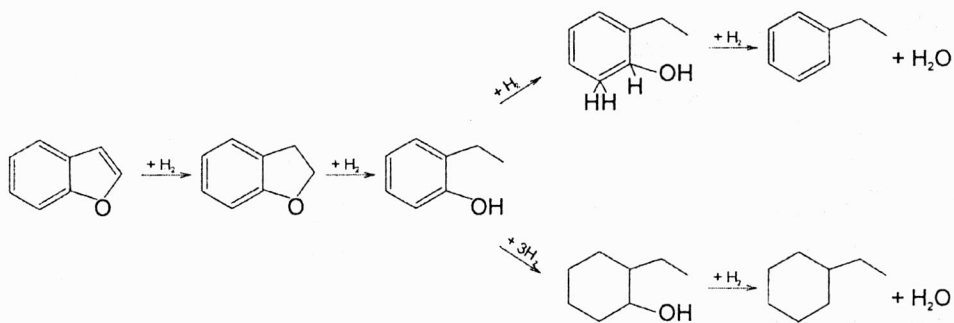


Fig. 3. Reaction pathways of HDO of benzofuran [12]

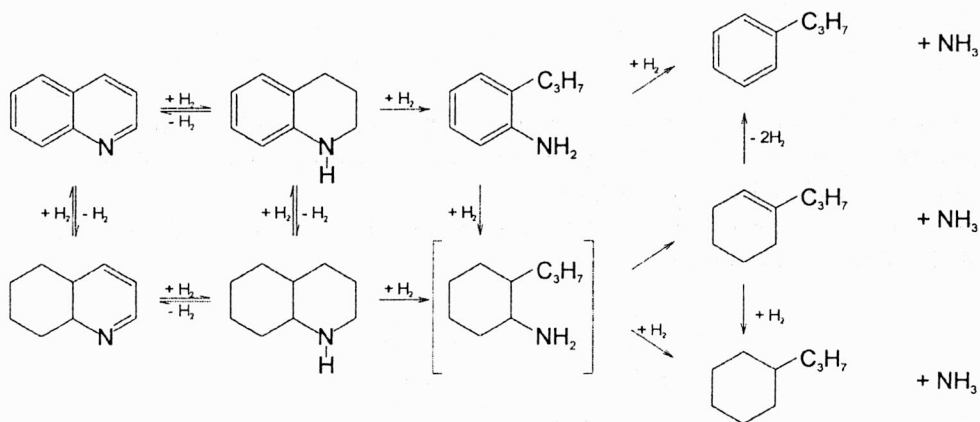


Fig. 4. Quinoline HDH-reaction network proposed [11]

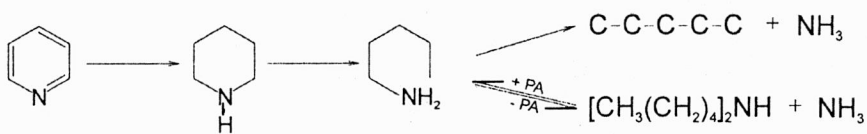


Fig. 5. Proposed mechanism for HDN of pyridine (where PA is pentyloamine) [6]

regeneration plant. The purified amine from the regeneration column is subjected again to the adsorption process; the sour water is recycled to the regenerator as reflux, whereas the sour gas is directed to the sulphur recovery plant. The liquid phase from the high-pressure hot separator flows to the low-pressure hot separator and, after light hydrocarbons are stripped away, it is directed to the steam stripper which separates the liquid and gaseous distillates from one another and the hydrated (water-containing) hydrosulfinate. The hydrosulfinate is then dried in a vacuum drying column and, after being cooled, it is directed to storage tanks as finished product.



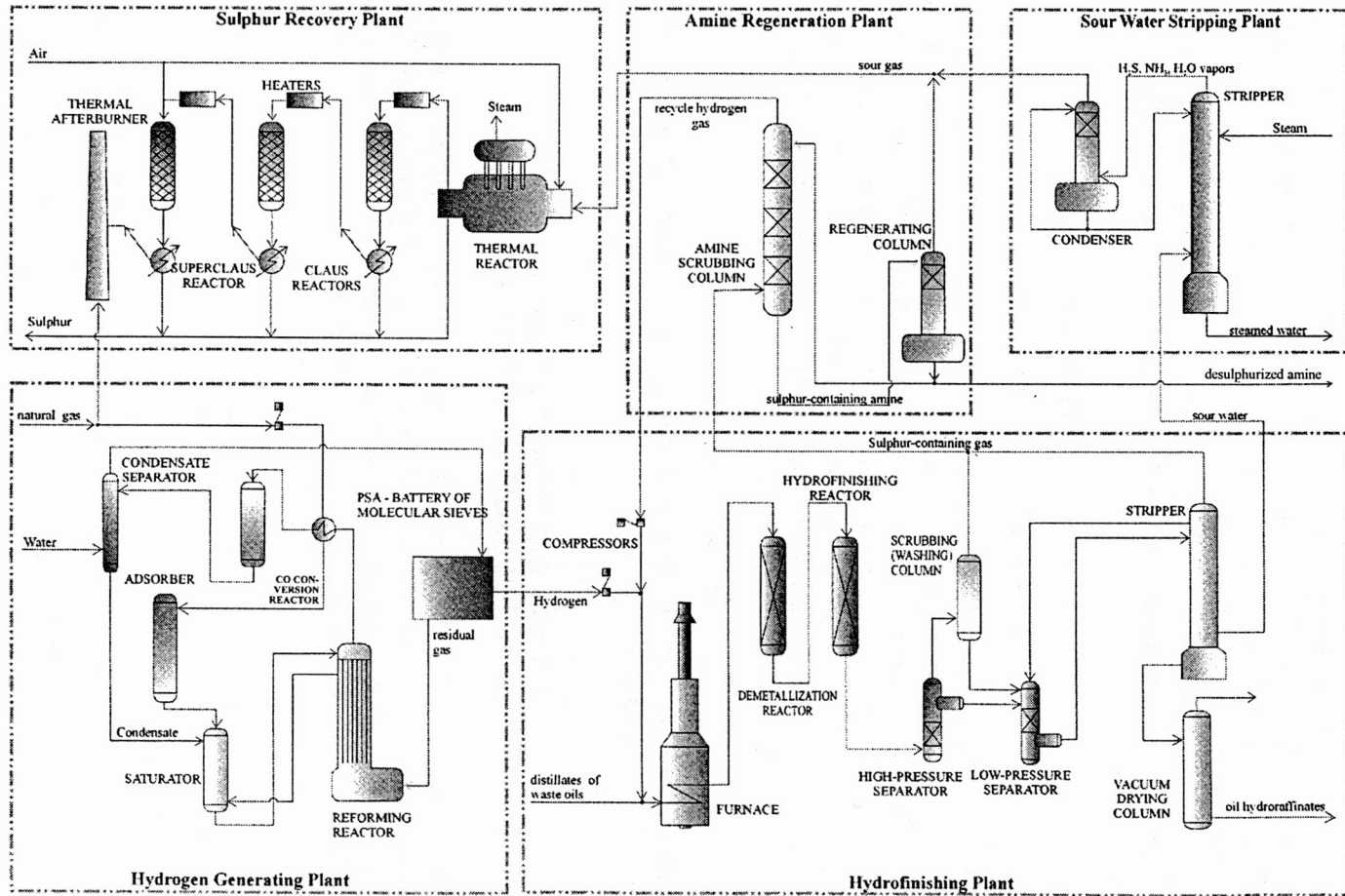


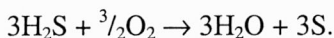
Fig. 6. Flowchart of plants making up the “waste oil hydrofinishing” complex in Jedlicze Petroleum Refinery

The sour water which is produced in the process is continually (uninterruptedly) directed to the sour water stripper plant. The plant serves to obtain water of such qualities which make it suitable for further treatment in the wastewater treatment plant and gas suitable for treatment in the sulphur recovery plant.

The sulphur recovery process includes thermal combustion, two catalytic stages of the Claus reaction, the third catalytic stage of Superclaus and thermal afterburner. The streams containing H<sub>2</sub>S are mixed with air and subjected to combustion. The following reactions occur:



The precipitating sulphur is condensed in the steam heater. At this stage, ca. 60% of sulphur contained in the feedstock is recovered. The gas leaving the heater still contains a substantial amount of H<sub>2</sub>S and SO<sub>2</sub>. Further transformation towards recovery of 95% of sulphur proceeds in two reactors with high-reactivity catalysts. The feedstock stream is heated up to the temperature suitable for catalytic conversion. In order to recover 98% of sulphur from the feedstock, it is necessary to have the third catalytic stage – direct oxidation of H<sub>2</sub>S into S:



The flowchart of the hydrofinishing plant being in operation in Jedlicze Petroleum Refinery is shown in figure 6.

## 5. MASS AND ENERGY BALANCE OF THE HYDROFINISHING PLANT

The mass and energy characteristics of the hydrogen unit in Jedlicze Petroleum Refinery was prepared on the basis of real flows in July 2002. The operation of all the units in the hydrofinishing complex was stable and the load of the plant was about 70%. In table 2, the flow rates of feedstocks and products are shown, while in table 3,

Table 2

Mass flows in the hydrofinishing plant in July 2002

Specification		Volume
1	2	3
Feedstocks	sulphur-containing spindle oil	1.000 t <sub>feedstock</sub>
	natural gas for reaction	0.023 t/t <sub>feedstock</sub>
	boiler water	0.150 t/t <sub>feedstock</sub>

1	2	3
Products	oil hydroraffinate	0.961 t/t <sub>feedstock</sub>
	sour liquid distillate	0.006 t/t <sub>feedstock</sub>
	wastewater and oily slops	0.112 t/t <sub>feedstock</sub>
	sulphur	0.003 t/t <sub>feedstock</sub>

The balance does not include the utilities recycled to the plant, i.e., sour water and fuel gas containing sulphur.

Table 3

The indicators of consumption of energy utilities  
in the hydrofinishing plant

Energy utilities	Indicator of consumption
Electric power	58.51 kWh/t <sub>feedstock</sub>
Medium pressure steam	333.06 kg/t <sub>feedstock</sub>
Low pressure steam	251.90 kg/t <sub>feedstock</sub>
Nitrogen (contaminated)	6.09 kg/t <sub>feedstock</sub>
Nitrogen of high purity	4.15 kg/t <sub>feedstock</sub>
Technical air	—
Instrument air	8.56 kg/t <sub>feedstock</sub>
Cooling water	62.50 kg/t <sub>feedstock</sub>
Natural gas for combustion	51.64 kg/t <sub>feedstock</sub>

the indicators of the energy utilities are collected and expressed in proper units per 1 MT of feedstock, the utilities being necessary for hydrofinishing of spindle oil coming from the vacuum distillation column.

## 6. OIL RAFFINATES QUALITY

The objective of the hydrofinishing plant being in operation in Jedlicze Petroleum Refinery is to improve the physical and chemical properties of the feedstock oils coming from the distillation of waste oils but the distillates from crude oil may also be the feedstock. At a proper temperature and under proper pressure, the heterocyclic compounds, due to their contact with hydrogen in the presence of the catalyst, are transformed into by-products such as H<sub>2</sub>S, NH<sub>3</sub>, H<sub>2</sub>O and HCl. In this way, olefins and also partially naphthene and aromatic hydrocarbons are saturated. This results in an improvement of colour, increase in oxidation and thermal resistance and stability of oil. Apart from the improvement of the properties of feedstock oils the desulphurization of oils also takes place to the level of 0.5% wt, which creates the possibility of producing highly-desulphurized fuel oils and base oils of the quality comparable to that of feedstocks obtained from processing virgin (crude) oil.

Table 4 compares the essential properties of fuel oil and machine oil. The listing includes the cuts after regeneration in the vacuum distillation unit, which then were treated in the hydrofinishing process.

Table 4

Comparison of essential properties of the two oil cuts

Selected parameters of oil cuts	Fuel oil II		Machine oil	
	After distillation	After hydrofinishing	After distillation	After hydrofinishing
Density [g/cm <sup>3</sup> ]	0.873	0.860	0.877	0.871
Viscosity at 40 °C [mm <sup>2</sup> /s]	12.7	11.02	41.3	37.4
Coke [%]	0.03	0.005	0.017	0.012
Ash [%]	0.002	0.001	0.002	0.001
Sulphur [%]	0.58	0.022	0.56	0.075
Acid number [mg <sub>KOH</sub> /g]	0.54	0.016	0.096	0.017
Colour acc. to Lovibond	6.5	0.5	over 8	1

The properties of distillates depend not only on the parameters of the process, but also on the characteristics of oils being regenerated and the way in which they have been collected, since each batch of waste oil has different composition and thus different properties. The comparison of oils after high-pressure distillation to those after hydrofinishing shows the content of sulphur to have substantially decreased: in fuel oil 26 times and in machine oil 7 times, respectively. As a result of hydrofinishing, the acid number lower than 0.02 mg<sub>KOH</sub>/g was obtained, the content of ash was decreased twice in both cuts and the content of coke was reduced (6 times in fuel oil). Low indicators of colour prove good reduction of resin compounds. The results explicitly show the dramatic increase in quality in comparison to the previously existing technology. The related cost are high. Apart from the investment costs, the costs of additional feedstocks and energy consumption are added. The emissions of CO<sub>2</sub> and SO<sub>2</sub> to the atmospheric air are also higher, which is caused, first of all, by higher consumption of energy utilities. However, the reduction of sulphur content in the final product and the improvement of the product quality are worth the cost. It can be inferred from the mass fractions of sulphur (table 4) that in the 30 MT of fuel oil produced annually by Jedlicze Petroleum Refinery, the content of sulphur in the oil, after the hydrofinishing process, is reduced even by as much as ca. 160 MT. Thus, annually, 160 MT of sulphur in a dispersed form shall not be emitted from diesel engines to the air due to combustion of fuel oil coming from reprocessing of waste oils. Another advantage is that oils with low sulphur content meet the EU standards and may be sold on world market.

## 7. SUMMARY

The most rational and ecologically advantageous way of the waste oil treatment is conservative recovery of base oils contained in the WO by removal of used additives and products of decomposition and coking present in the oil after their use. In order to be able to obtain the re-refined base oils of the quality required at present and in the future, it is necessary to apply state-of-the-art regeneration techniques. Taking into consideration users' requirements as regards quality and the increasing complexity of composition of engine oils, hydrofinishing seems to be the most effective finishing step. It aims at reduction or removal of residual metals and metalloids, organic acids, and compounds containing chlorine, sulphur, and nitrogen. The high-temperature and high-pressure process also reduces the content of PAH to the acceptable level. There is a perfect comparability between re-refined base oils and the virgin base oils (from the first processing of crude oil), but, in spite of that, some engine manufacturers still reluctantly accept recycled products.

In the EU countries in the year 2000, ca. 1.8 mln MT of waste oils was collected, 26% of which were re-refined as recommended by law [13]. In the Polish circumstances, waste oils may be re-refined to base oils only in Jedlicze Petroleum Refinery. Assuming the annual level of collection of ca. 150,000 MT of waste oils and using the whole processing capacity of the plant in Jedlicze, it is possible to re-refine 53% of collected oils.

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#### HYDRORAFINACJA DESTYLATÓW OTRZYMYWANYCH Z OLEJÓW PRZEPRACOWANYCH

Przeanalizowano proces hydrorafinacji olejów pracowanych po destylacji wysokopróżniowej. Proces ten prowadzi do redukcji związków organicznych zawierających azot, tlen, siarkę i metale. Na podstawie przykładowego bilansu produktów pokazano poprawę istotnych parametrów baz olejowych po obróbce oleju wodorem. Wykazano znaczne obniżenie ilości siarki emitowanej wraz z gazami spalinyowymi silników wysokoprężnych, które spalają olej napędowy poddany procesowi hydrorafinacji.