### OIL AND GAS REFINING

# From Carpathian gasoline plants to the modern petroleum industry of Ukraine

УДК 665.63:665.637.64

#### M.M. Bratychak

Dr. of chem. sciences

Lviv Polytechnic National University

## *The paper describes the origin of petroleum refining industry and the current state of oil refining in Ukraine.*

Petroleum industry emerged and developed in close cooperation with the extraction and consumption of oil and its processing products. The information on availability of oil in the Carpathian region has long been reflected in the geographical names of areas as Ropa, Ropyanka, Ropytsya etc., where the oil deposits came to the surface.

Up to the early nineteenth century oil has not gained wide use in the economy of ancient Galicia and in the world. Arguably, only the primitive methods of oil extraction and processing existed. It went about the various primitive techniques for extraction of thickened oil (without light components), which was used to grease the axles of carts. It was important during the widespread use of horse transport, but the commercial use oil was secondary. Only in 1810 the Austrian Government recognized oil and mineral wax the as raw material subject to the mining monopoly. Accordingly, it became necessary to obtain the permit for oil and wax extraction from the Department of Mining, located in Drogobych.

In the first half of the nineteenth century the interest in oil is growing, which soon was expected to have an important role in the further development of civilization, which is caused solely by the industrial revolution started in the second half of the eighteenth century.

This process, which later became worldwide, was initially stimulated by the need to find substitutes for scarce vegetable oils and animal fats, used for lighting in cities which were growing quickly due to industrial development and population growth.

The first attempts to obtain the product fit for lighting from oil and introduce the same for massive use were made in 1816 - 1817 in Galicia by J. Hecker and J. Mitis. The oil distillate resulting from petroleum distillation (in the way which is now forgotten) was used for lighting of streets in Drogobych and military barracks in the town of Sambir. Thereafter the production of distillate (lighting kerosene) was expanded. From the memoirs of a pharmacist, J. Zeg in the Almanac of a pharmaceutical association for 1889 it is known that the slave of Baytal performed the oil processing in 1830 in the village of Naguyevychi. For this he used a metal container with an attached stream from the gun cooled with water. He also received three fractions: gasoline, kerosene and bottoms. The gasoline and kerosene fractions were sold by him to Galician pharmacies and the bottoms was used to grease the wheels.

The second half of the nineteenth century was remarkable for the rapid growth in demand for lighting, as well as fuel to propel the steam engines. In this regard, all countries which at that time were mining, oil almost simultaneously intensified their activities towards the development of lighting kerosene. I. Lukasyevych was the first who achieved the positive results, which became crucial to the creation of oil extracting and refining industry. In 1853, I. Lukasyevych working as a pharmacist in Lviv pharmacy "Under a gold star", owned by Mr. Mikolyash, together with Jan Zeg,

obtained the kerosene which was suitable for the practical application by its properties, i.e. for lighting. This product (which they named camhene or new camphene) with the boiling point of 200-250°C was isolated from the distillation with a broad margin of boiling, previously obtained from oil by extraction of lower and higher boiling components by fractional distillation. Camphene was purified with sulfuric acid and sodium hydroxide. It was safe to use for lighting in the lamp of new design developed by I. Lukasyevych with a Lviv tinman, A. Bratkovskyi.

Mikolyash, Lukasyevych and Zeh Partnership entered into an agreement with a public hospital in Lviv on its lighting with kerosene lamps, pursuant to which they delivered 500 kg of kerosene and Bratkovsky supplied the required lamps to the hospital. On July 31, 1853 Lviv hospital was lit, where the first complex surgery was made at night by the light of kerosene lamps. This day went into history as the beginning of the world oil industry.

At the beginning of the second half of the nineteenth century Drogobych becomes a large, and subsequently the largest refining center in Galicia. In the late 19<sup>th</sup> and early 20<sup>th</sup> century the new oil (or as they were then called "gasoline") plants in Boryslav, Ulatovychi, Sambir, Stryi, Lviv appear in Galicia. In 1879 there were 36 plants registered, and after 10 years there became 57 of them. They produced 20,400 tons of petroleum products a year, and after 6 years their capacity reached 41,000 tons a year. These factories employed over 2,000 workers. As a result of this development, Galicia temporarily becomes the third after Russia and the United States world-class center for oil extraction and processing.

The first refinery in Drohobych was founded in 1859 by A. Schreiner. It was a small company which burned down later on. However, in 1863 a new joint venture of two owners G. Altman and J. Gottlieb was created at the same place, which has become the basis for the modern NPK-Galychyna OJSC (formerly Drogobytsky oil refinery). This plant later on was called Galicia. Therefore, the year of 1863 is rightly considered the beginning of the industrial re-working of oil in Ukraine.

In 1914, at Galicia refinery there were two oil refining installations, a periodic one, consisting of seven cubes, and a continuous, with twenty boilers, six of which are operated at atmospheric pressure, and three under reduced pressure (300 mm Hg). At installation of the periodic oil refining there were two cubes which carried out the filtrate distillation (obtained from paraffin oil), making it possible to extract the lubricating oil of the required quality. All this was provided by three bitumen cubes and ten cubes of thermal cracking.

During the interwar period Galicia refinery was built up to the capacity close to 140 tons a year, and in 1925 there was built Cross installation for thermal cracking, similar to that existing at the Vacuum Oil Company in Chekhovychi. This plant was the first in Poland which started manufacturing bitumen named Molfalt and Gambit. Its oils sold under the Galtol brand name worked well in the market.

Searching for the ways to use and sell oil discovered in Galicia, the extraction volumes of which were growing rapidly, the management of the National Oil Company in 1902 considered the issue of the beginning of petcoke for locomotives of Austrian railways. This led to the construction of a new refinery, which in 1919 was named Polmin.

In 1938, Polmin first introduced engine oil called Triselektol with viscosity index close to 100, obtained by selective refinement of oils with cresol, to the market. At the same time it was planned to build a plant for selective refinement of oils with furfural. The installation for oil treatment with sulfuric acid using centrifuges (making the cleaning process continuous, and reducing the consumption of acid), as well as a plant for calcium oil production were built too.

Introduction of a two-stage tubular installation distillation for oil distillation at Polmin significantly affected the increase in output, primarily the expansion of the range of bitumens, including for road, which were manufactured there. This method of oil distillation allowed obtaining the vacuum residue with stable properties and deep elimination of light fractions. These restudies were the raw material for the production of commodity road and industrial bitumens, and sometimes just finished products of this type.

In September 1939, both refineries in Drogobych were nationalized and became state property. The name of Polmin was changed for Drogobytska refinery No. 1, and Galicia for Drogobytska refinery No. 2.

Refining in the heart of oil extraction, i.e. in Boryslav, dates back to 1899, since the Galician oil company successfully drilled four wells with oil production of 40 t/h.



Figure. Dynamics of oil processing in Ukraine, mio t

At early 1902 the citizen of Boryslav, Kornhaber, buys 0.25 hectares of land near the village of Hubachi (now a part of Gallak OJSC). This area was not chosen by chance; nearby there was the railroad which connected Boryslav with Drogobych. Three cube containers with the capacity of 0.5 m3 each are installed and the kerosene and gasoline production is started.

In 1910, the Refinery buys another 5 hectares of land and, having made use of the cheap oil, installs the distillers, which provided an opportunity to obtain the liquefied petroleum gas, gasoline, diesel fuel, paraffin oil and paraffin from petroleum. From Skhidnytska oil they produced the cylinder oil as coke waste. However, thereafter Refinery was behind Galicia and other refineries in Boryslav by its technical equipment.

The primitivity of technologies used at the Refinery can be demonstrated by paraffin production. The paraffin oil driven off from oil was poured into wooden barrels, which were buried in the ground for 2 to 3 months. After then the paraffin was pressed by hand presses in sacks. Thus obtained black wax sent to refineries for further processing. At the end of 1938 the plant operated for only one month a year, and for the remainder of the time (11 months!) it was in conservation.

In 1896 Lviv refinery was built. The owners of the refinery were Liansberg, Val, Baron, and since 1920 the Joint Stock Company of Oil Industry and Terrestrial Gas in Ukraine, founded by the Polish Regional Bank and Polish Industrial Bank. The plant occupied an area of 4.33 hectares, which housed the factory building, distillation, alkaline and acid installations, collections for gasoline, kerosene, heavy oils and oil, a warehouse of candles and paraffin, a room for workers and two houses. At the plant there were 11 small cubes 10 m3 each for rectification of oil, 13 machines for manufacturing of candles, a melting pot for paraffin and a generator to produce own power. In the boiler room there were two steam boilers. After plant expansion the oil distillation was carried out in two cubes 50 tons each. The process was organized in such a way that the oil field (in %): gasoline factions - 20, kerosene - 20, diesel fuel - 20, oil, engine oil - 15 and cylinder oil - 18. The distillation of gasoline fraction was carried out in the boiler with the capacity of 26 m3. The output products were heated by water vapor. Through coils, fractional columns and refrigerators the gasoline went into collections with a capacity of 170 m3. The plant had six such collections.

The kerosene passed the acid-alkaline purification in mixers with a capacity of 37 m3 each. Waste acid with asphalt were used in mixtures with coal as the energy fuel in the distillation cubes. The engine and cylinder oil was purified by acid-base method in two machines with mixers with a capacity of 28 m3 each. The performance of the oil treatment process was 21 tons a day.

The year of 1931 became crucial for the plant because, according to the latest achievements of contemporary technology, the construction of the tubular system of Foster Willer system installation was commenced. This setting was to replace the old distilling equipment. The tank fleet also underwent the reconstruction.

After commissioning the Foster Willer unit worked for 14 days in ambient and for 14 days in vacuum mode for processing the heating oil and then repeated cycles.

In 1932 the plant began construction of the emulsions workshop, consisting of 80% refined and deodorized gasoline, 18.5% water and 1.5% emulsifier and intended for the chemical industry. The year of 1934 was remarkable for construction of facilities for oil dispensing and installation of filter presses. To improve the quality of gasoline obtained in distillation columns, it was mixed with ethanol, thus obtaining the so-called "gas-alinizine." In the same year the oil dewaxing plant was built. The plant water infrastructure also underwent reconstruction.

In 1939, after the consolidation of Ukrainian lands, the oil refineries were nationalized.

In 1897 the refinery was built in Nadvirna to process the crude oil from the surrounding villages Bytkiv, Pasichna, Kosmache etc. The oil is also brought in tanks from Boryslav.

In the 30s' of the twentieth century the refinery in Nadvirna changed its owners several times. They were Romanian, French, Italian and British businessmen.

The oil was carried by its distillation in cubes with the capacity of 10 m3 each. Given that the oil Bytkivske deposit contained much paraffin, had a high setting point and was the main raw material, the plant only worked in summer. Five of the seven existing units worked simultaneously. The units were heated with wood or sawdust soaked in fuel oil. Such a cube installation yielded gasoline (end boiling point 225°C), kerosene (end boiling point 350°C) and fuel oil. The kerosene thus obtained was purified with sulfuric acid and alkali and rinsed with water. All transactions involving the supply of acid, alkali, water and mixing were carried out manually. The installations with mechanical mixing were introduced in the plant only in 1927-1928.

In 1936, for obtaining of paraffin oil, two large cubes with reflux were installed in the factory. The paraffin shop with the capacity of 40 tons per month was built. The paraffin oil was taken up to 400°C, which then yielded hard paraffin and diesel. In the paraffin plant there were four crystallizers and three filter-presses. The flowchart of paraffin obtaining was not fundamentally different from the standard one. In 1937-1938 the plant processed 750 tons of oil per month. At the end of 1938 its capacity reached 1,000 tons per month. In September 1939 the oil refining plant in Nadvirna, like all Carpathian plants, was nationalized. In 1940 here another cube of 24 m3 was installed and the plant capacity increased up to 1150 tons of oil a month.

In the territory of eastern Ukraine's the oil refining industry was initiated by cracking plant construction in Odessa (1935), Berdyansk (1936) and Kherson (1937).

During the postwar years two modern refineries were built in Kremenchuk and Lysychansk, and the plants in Drogobych, Lviv, Nadvirna, Odessa and Kherson were reconstructed and expanded, which promoted the increase of design capacities related to oil processing, the scope of which reached 62.5 mio tons a year in 1990 (table 1).

Table 1

Capacity of Ukrainian refineries related to initial processing of oil, million tons a year

Refinery	Designed capacity in 1990	Technical capacity in 2012
LINIK PJSC, Lysychansk	23.5	8.0
Ukrtatnafta PJSC, Kremenchuk	18,5	8.0
Khersonnaftopererobka PJSC, Kherson	8.7	-
Lukoil ONPZ PJSC, Odessa	3.9	2.8
NPK-Galychyna PJSC, Drogobych	3.9	1.8
Naftokhimik Prykarpattia PJSC, Nadvirna	3.5	2.0
Lviv Research Oil and Lubricant Plant PJSC, Lviv	0.5	-
Total	62.5	22.6

The oil and gas condensate can be processed in Ukraine at six refineries, Lysychansk, Kremenchuk, Odessa, Kherson, Drogobych and Nadvirna, as well as five gas distillation plants, the largest of which is Shebelynskyi and three units for processing the hydrocarbon feedstock. There are also about 20 mini-refineries with the total capacity up to 400 tons per year.

The Ukraine refineries had or have various technological installations, the processes at which are described in Table 2.

Table 2

Pafinary	Technology installations
Kremenchuk	Primary processing, catalytic reforming, catalytic cracking, hydrotreating of reactive and diesel fuels, selective clearing, dewaxing, hydrotreating of distillates, hydrotreating of paraffin, hidroizomerization of diesel fuels, MTBE production, bitumen production
Lysychansk	Primary processing, catalytic reforming, catalytic cracking, isomerization, hydrotreating of diesel fuels, production of MTBE, polymerization of propylene,
Kherson	Primary processing, catalytic reforming, coking, bitumen production
Odessa	Primary processing, catalytic reforming, catalytic cracking, isomerization, hydrocleaning of reactive and
Drogobych	Primary processing, thermal cracking, catalytic reforming, coking, of producing bitumen
Nadvirna	Primary processing, catalytic reforming, coking

Technology processes at Ukrainian refineries

The reduction of oil processing in Ukraine (figure) led to the elimination of certain processes at refineries and suspension of production, particularly at the Kherson refinery.

The decline in oil processing in 2006 was associated with downtime of Odessa and Kherson refinery due to their modernization. In addition, this process was affected significantly by sharp rise in world oil prices and higher excise duty on Russian oil, which from \$ 35 per ton in 2004 increased to \$ 250 per ton in 2006. Under these conditions, at a relatively low depth of oil processing at Ukrainian refineries, the oil export has become more profitable for Russian oil companies. The increase in the world oil prices also played a positive role in the development of the Ukrainian oil extraction and increase of the oil depth processing parameter at all existing refineries.

2010 2011 Refinery 2009 3119.0 Kremenchuk 3121.8 3611.9 Lysychansk 4952.8 4811.5 4946.4 Kherson Odessa 2051.6 1488.4 Drogobych 422.9 373.0 165.7 Nadvirna 155.3 195.9 137.8 Shebelyno 659.9 680.28 10771.4 9049.18 Total 11140.6

#### Oil processing at Ukrainian refineries, thousand tons

After analyzing the data of table 3 we wondered why the Ukrainian oil refiners in 2011 lost nearly a fifth of the volume of oil. The main reasons include the higher oil prices and lack of support from the state. In March 2011 a memorandum with refinery owners was signed, but the state almost defaulted.

In Ukraine today there are left two plants which may produce oil; the western factories do not work. Odessa Lukoil was unable to defend its assets, and therefore stopped the production. The situation with the reconstruction of Kherson refinery is unclear.

Working in market conditions, and Kremenchuk and Lysychansk refineries began solving their immediate problems independently. Ukrtatnafta PJSC chose the path of reduction of its production 15% and cutting down the imports of Azeri oil. LINIK PJSC decided to leave the production of no more than 50 to 90 thousand tons of light products in Ukraine.

Still it is worth noting that Ukrtatnafta PPSC launched the production of gasoline with improved performance (Euro-4) in 2011, which was possible due to the upgrade of the hydrotreatment unit of section 200 of installation JIK-6y for hydrotreatment of catalytic cracking gasoline. Due to the construction of dewaxing installation jointly with Shell Criterion, which gave the company an opportunity to produce 70 to 90 tons of winter and arctic diesel fuel monthly, we managed to survive the cold winter of 2012. The building of installation for isomerization of light gasoline fractions and hydrotreatment of catalytic cracking with the capacity of 380 and 600 tons respectively by Ukrtatnafta PJSC will give the opportunity to obtain gasoline with a sulfur content less than 10 mg/kg and aromatics content not more than 35%.

In 2011, from among all refineries of Ukraine, the Lysychansk LINIK looked most attractive. Loading with primary processing per month amounted to 350-450 thousand tons. The plant is producing gasoline of Euro 4 standard and plans to produce Euro 5. Since September 2011 the company produces diesel fuel with a sulfur content of 10 ppm. Now such diesel (Standard 5) accounts for 30% of the total diesel fuel produced.

The perspectives of Lukoil ONPZ JSC are not defined. In 2005-2008, the production suspension was caused by the plant reconstruction. In 2008-2010, the plant produces the products which serve as raw material for the Balkan enterprises of Lukoil. In the future, maybe, it will work on Azeri oil. NPK-Galicia and Naftokhimik Prykarpattia reduced the volume of oil refining almost twice. Some local oil is forwarded to Ukrtatnafta PJSC. The oil from Azerbaijan turned out to be too expensive for these companies too. The reconstruction works are frozen and the staff is dismissed.

As regards Kherson refinery, it is not working for more than six years already. The plant undergoes a complete reconstruction. It is hoped that in 2015 the plant will work and produce Euro 5 standard.

The author believes that only through joint efforts of the owners of enterprises referred to

herein and correct state policy for the introduction of import duties on petrochemicals we can overcome the crisis in the Ukrainian oil processing.

#### References

1. **Нафта** і газ Прикарпаття. Нариси історії: монографія // Під ред. Ю. Зарубіна. – Краків–К.: Наук. думка, 2004. – 570 с.

2. Historia polskiego przemyslu naftowego / Під ред. Р. Вольвови- ча. – Вгzozów-Крако́w, 1994. – Т. 1. – 749 с.

3. **Братичак М.** Проблеми та перспективи нафтогазової промис- ловості України / М.М. Братичак // Тези доп. VI наук.-техн. конф. «Поступ в нафтогазопереробній та нафтохімічній промисловості», Львів, 25–28 квітня 2012 р. – Львів: Видавництво НУ «Львівська політехніка», 2012. – С. 6.

4. **Братичак М.М.** Від газолінових заводів Борислава до сучасної нафтопереробної промисловості України / М.М. Братичак // Тези доп. на міжнар. наук.-практ. конф. «Стан, проблеми та перспек тиви нафтової промисловості України», Борислав, 7–9 вересня 2012 р. – Львів: Видавництво НУ «Львівська політехніка», 2012. – С. 17.

5. **Братичак М.М.** Нафтова і газова промисловість України: про- блеми і перспективи / М.М. Братичак, П.І. Топільницький // Мат. IV Міжнар. наук.-техн. конф. «Проблеми хіммотології», Рибаче, Крим, 24–28 вересня 2012 р. – Одеса: Астропринт, 2012. – С. 23.

#### Author of article



#### Bratychak Mykhaylo Mykolayovych

He graduated from the Faculty of Technology of Organic Substances of the Lviv Polytechnic Institute, Doctor of Chemical Sciences, Professor, Academician of UNGA.

Since 1994 he has been working as a manager of department of chemical technology for oil and gas re-processing of the Institute of Chemistry and Chemical Technology of the Lviv Polytechnic National University (Lviv).