CHEMISTRY

DOI: https://doi.org/10.36719/2707-1146/46/28-33

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THE OIL REFINING INDUSTRY IN AZERBAIJAN AND A BRIEF HISTORY OF THE DEVELOPMENT OF THE CATALYTIC CRACKING PROCESS

Azerbaijan is a country rich in oil in all periods of its history. This is a country that is considered the home of ”black gold “, known as one of the leaders in oil extraction in the world, rich in material and spiritual resources, as well as having the oldest experience in the field of oil extraction.

The article talks about the history of the creation and development of chemistry and petrochemical science in Azerbaijan in ancient times, as well as the process of oil extraction and processing as well as the interest of foreign oil companies in this field and investment for the development of the oil industry in Azerbaijan.

In addition, the works of Russian scientists living in Azerbaijan in this field and the most important results of the fundamental research conducted by Azerbaijan scientists in the development of the oil industry are briefly presented.

In the development of the catalytic cracking processes, which is one of the processes of the oil industry, the fundamental scientific research works oil Azerbaijani scientists and the Institute of Petrochemical Processes named Academician Y.H.Mammadaliyev, the ancient science temple of Azerbaijan, which carries out these works, are mentioned.

Today, the oil industry of Azerbaijan is conquering higher peaks in terms of more efficient use of oil, our natural resource. For the sake of the bright tomorrow of our people.

Keywords: *oil refining, catalytic cracking process, oil wells, fluidized bed, small-dispersed catalyst*

Introduction

In Azerbaijan, the history of chemical concepts is very ancient. As in some other Eastern countries, the emergence of the science of chemistry in Azerbaijan traces its origins to the extraction of ore and the processing of metals. Metallurgy, one of the important industrial sectors, is in turn associated with chemical transformations.

To determine the history of the science of chemistry in Azerbaijan, recent archaeological excavations have studied a large number of material-cultural artifacts from the Eneolithic, Bronze, Iron Ages, and the Middle Ages. These studies indicate that the use of metals began at the end of the 4th millennium BCE and the beginning of the 3rd millennium BCE. According to archaeologists, the first metal known to the ancient population of Azerbaijan was copper.

In the Lesser Caucasus mountains located in the territory of Azerbaijan, copper deposits exist, and the methods of extracting copper were known to our ancient ancestors. It has been discovered that in the 2nd millennium BCE, a high bronze culture existed in Azerbaijan, and the Iron Age began in the 1st millennium BCE. Important ancient iron ore deposits were found in Karabakh, particularly near the village of Bayan in the Ganja region. The famous historian Hamdallah Qazvini also provided information about this. In the territory of the ancient Azerbaijani state of Manna, copper, gold, silver, and other metals were extracted. The Albanian historian M. Kalankatuklu wrote: "This country has all kinds of useful minerals. Gold, silver, copper, and pure clay are extracted from the mountains."

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extraction of ore and the processing of metals. Metallurgy, one of the important industrial sectors, is in turn associated with chemical transformations (M.İsmayılov Bakı-1993.səh.246-249).

In the Middle Ages, the development and spread of applied chemistry in Azerbaijan had a positive impact on the science of medicine. At that time, medicines prepared based on petroleum, mercury, sulfur, and other substances, in addition to plant-based drugs, were used in medicine.

Notable medieval scholars significantly contributed to the development of chemical science in Azerbaijan: the famous physician and chemist Abu Ali Ibn-Sina, the encyclopedic scholar Nasreddin Tusi, and one of the founders of medicine and applied chemistry, Omer Osmanoghlu was one of the prominent philosophers, mathematicians, chemists, and physicians in Azerbaijan in the 12th century.

The creation and development of chemical science and industry in Azerbaijan, as well as the importance of our valuable natural resource oil are of great significance. The history of oil extraction in Azerbaijan is ancient. Azerbaijan has long been famous as the "land of black gold" and the "land of fires." The first information about the production of oil and its various uses in Azerbaijan is found in the works of the 10th-century Arab scholar and traveler Masudi. In ancient times, oil was mainly used as fuel and a medicinal agent (Khalilov, 1990: 8-45).

In the last hundred years, due to its geographical location in the South Caucasus region, the exploitation of its rich oil and gas reserves, and the implementation of large-scale projects for their export to world markets, Azerbaijan has become a geopolitical center where the interests of the USA, European, and Asian states intersect.

Thus, the oil industry of Azerbaijan has become an important element of its economic and political life. For the first time in the world (eleven years before the USA), an oil well was drilled using technical means in Azerbaijan in 1848 by Russian engineer Semyonov. After this, in 1863, a well was drilled on Pirallahi Island using mechanical methods. In 1869, when master Allahyar drilled a well mechanically in Balakhani, a loud noise at a depth of 10-15 meters scared the workers, leading them to fill the well. Three years later, in 1871, a well was drilled using technical methods in Balakhani, producing 45,000 poods (700 tons) of oil per day (Suleymanov, 1989: 64-75).

In the late 18th century and into the mid-19th century, German Baron Tornay laid the foundation for the production of kerosene (lamp oil) in Azerbaijan. In 1863, Baku engineer Javad Malikov pioneered the production of kerosene (white oil) for the first time. From the 1860s onwards, industrial-scale oil refineries began to emerge in Baku to meet the growing demand. By the late 1870s, there were nearly two thousand oil production facilities operated by various individuals and companies in Baku alone. It should be noted that during the 19th century, the Russian Empire primarily extracted oil from villages on the Absheron Peninsula, marking the beginning of Russia's oil industry.

In 1872, Baku villages produced 5 million tons of oil, and by 1900, this figure rose to 661 million tons, accounting for 95% of the oil produced in the Russian Empire and more than half of the world's total oil production. Additionally, kerosene (white oil) production reached 1,500 tons in 1873, and that same year, Baku technologist A. Tabrizov developed a continuous refining process for oil. By 1875, the volume of kerosene production in Baku had reached 847,700 poods (a Russian measure of weight), and by 1901, this number had increased to 2.5 million poods (Süleymanov,1989: 64-75).

The shortage of oil production in Azerbaijan attracted the interest of foreign states. Major world powers competed for oil in Azerbaijan: American J. Rockefeller's Standard Oil, under the leadership of H. Deterding's Royal Dutch Shell from England, Rothschild's "Caspian-Black Sea" and "Mazut" from the French, and the syndicates of Swedish Nobel Brothers were all active in Baku. The development of the oil industry in Azerbaijan paralleled the role played by Standard Oil in the United States with the Nobel Brothers in Azerbaijan. They established a large-scale oil industry company called "Nafta" in Baku. The founders of this industrial firm were the Nobel brothers Ludwig, Robert, and Alfred, along with their friend Peter Bilderling. By the late 19th

ISSN: 2707-1146
e-ISSN: 2709-4189

century, this company, led by Ludvig Nobel, earned the title of "Oil King" in the Russian Empire. The Nobel Brothers, who owned the Baku oil refining plant, exported kerosene via the Caspian Sea to Russia's main industrial centers and abroad. At one point, this company controlled 50.1% of the sale of white oil in Russia, a figure that later reached 80.3% in different years.

In the 19th century, the development of oil extraction and refining industries in Azerbaijan was intertwined with the unique global economic system, subject to the technological processes of the era, both successful and unsuccessful. Azerbaijan not only matched the world level in terms of technology, scientific research, and equipment but excelled in many respects.

The development of the oil-chemical and oil refining industries in Azerbaijan is directly related to the scientific works and efforts of scientists and researchers tirelessly engaged in this field. Our scientific history shows that the work of researchers is never easy. It combines long-term scientific observations with tireless experimental searches.

The history of our science is rich with materials that illuminate the dedication, excellence, and profundity of scientific knowledge. It is crucial today to pay special attention to the study of the development of Azerbaijani chemistry and the oil-chemical industry. Just like in other fields, our primary task should be to introduce the younger generation to the scientists and servants of science who have contributed to this field, immortalizing their bright memories in history's annals for future generations and for the world.

The works of eminent scholars such acad. Y.H. Mammadaliyev, M.F. Nagiyev, V.S. Aliyev, H.H. Hashimov, S.J. Mehdiyev, R.S. Guliyev, M.I. Rustamov, B.A. Dadashov, I.M. Orujova, B.K. Zeynalov, S.A. Sultanov, F.I. Samedova, V.S. Qutiyarani, A. Mehdiyev, R.A. Aliyeva, V.M. Abbasov, A.J. Huseynova, E.T. Suleymanova, A.G. Azizov, V.H. Gasimov, M.A.Mammadyarov, and many others have significantly enriched the natural and technical sciences as well as the history of science among the humanities.

The valuable research, inventions, and discoveries in the field of petroleum refining, one of the leading areas of Azerbaijani chemistry, as well as their works discussing vital organisms, can be considered the most valuable source for the history of Azerbaijani chemistry and the oil-chemical industry.

Academician Y.H. Mammadaliyev's book "Development of Science in Azerbaijan," published in 1960, remains a valuable work in the history of science, maintaining its relevance and significance. In this book, Academician Y.H. Mammadaliyev demonstrated that the development of science in Azerbaijan began in the 12th century. He wrote, "... The Azerbaijani people have produced many eminent scholars, thinkers, and poets in their history. They have enriched world civilization and the brilliance of science with their outstanding works..."

Academician Y.H. Mammadaliyev then writes, "... Great thinkers of the 12th century include Abdulhasan Bakhmanyar ibn Marzban and Khalil Tabrizi. The distinguished astronomer of the 12th century, Fereydoun Ali ibn Abdul Karim Shirvani, the famous engineer and scholar Amiraddin Masud Nakhchivani, and the physician and philosopher of the 12th century, Afzaladdin Abdulmalik Khoja, have created valuable scientific works that have reached our era..."

In his book, Academician Y.H. Mammadaliyev provided extensive information about the scientific activities of Azerbaijani chemists, such as Movsum bey Khanlarov and teacher Sadig Huseynov (Məmmədəliyev, 1960: 10-25).

Over the years, both chemistry and the number of scientists working in this field have developed in Azerbaijan.

Academician V.S. Gutiryat, who lived in Azerbaijan for a long time, conducted precise theoretical and experimental research on various hydrocarbon conversion reactions involving alumosilicate catalysts. He developed the industrial method of catalytic cracking in the "fluidized bed" of the catalyst. During his early career, Academician V.S. Gutiryat succeeded in developing the steam phase cracking method and, shortly thereafter, in the mid-1930s (together with M.A. Dalin), he devised a new and advanced technological process for obtaining ethyl alcohol from natural gases, demonstrating effective industrial implementation.

The distinguished scientist V.S. Gutiryat worked for many years at the Azerbaijan Scientific Research Institute of Oil Refining named after V. Kuibyshev (currently the Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev of the Azerbaijan National Academy of Sciences), where he led one of the largest laboratories (12).

During his tenure in Azerbaijan, Academician V.S. Qutiryat authored several monographs, including "Cracking and Reforming of Petroleum Products with Participation of Alumosilicate Catalysts" (1944), "Purification of Thermal Reforming Distillates" (1946), and "Research on Catalytic Cracking of Products using the Fluidized Bed Technique" (1962), among others.

It is worth noting that during World War II, Azerbaijan's oil fields played a crucial role in supplying combat aviation fuel. The Azerbaijani scientists and engineers of that period introduced a number of new innovations in the oil industry, supplying high-octane gasoline technology. During that time, the Allied forces received 75 million tons of crude oil, 22 million tons of gasoline, and other petroleum products.

From 1941 to 1945, scientists at the Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev of the Azerbaijan National Academy of Sciences made numerous scientific inventions and discoveries.

Academician Y.H. Mammadaliyev's achievements in obtaining high-octane aviation fuel and explosive substances during the Great Patriotic War played a significant role in the victory over fascism (Khalilov, 1990: 8-45).

During the war years, Professor Ali Guliyev led a group of scientists who prepared appropriate recipes for obtaining explosive substances and produced incendiary bulbs in large-scale facilities (Khalilov, 1990: 8-45).

In the 1960s and 1970s, under the leadership of academicians V.S. Aliyev and M.I. Rustamov, extensive research was conducted on improving the catalytic cracking system with a "fluidized bed" possessing a narrow-dispersed catalyst, as well as intensifying catalytic cracking of petroleum feedstocks.

Academicians V.S. Aliyev and M.I. Rustamov developed and implemented advanced, highly efficient catalytic cracking systems in Azerbaijan. They introduced a new catalytic cracking system with a "half-direct flow" and applied a reactor with an elevated catalyst flow in its first stage. The gas dynamics, technological, and thermal characteristics of these half-direct flow and two-stage catalytic cracking systems were thoroughly studied by the authors.

For the purpose of obtaining mono olefins, they worked on the catalytic dehydrogenation process of C_4-C_5 paraffin hydrocarbons for the first time worldwide using the K-5 narrow-dispersed catalyst in a fluidized bed. This process significantly reduced the production of divinyl from synthetic rubber by about 35% relative to its yeast value and reduced capital investment in plant construction by 40-50%.

The industrial application of this process yielded significant economic benefits amounting to millions of manats annually. Moreover, this process was implemented in synthetic rubber plants in various locations including Sumgayit, Sterlitamak, Kuibyshev, Omsk, and Romania during the former Soviet Union period.

Under the leadership of Academician V.S. Aliyev, these valuable research findings and the technological processes developed based on them enabled the creation of a solid material base for producing high-quality motor fuels. His research also contributed to increasing the reserves of petroleum residues and heavy oil fractions in addition to distillate petroleum feedstocks (Aliev, Indyukov, Efimova, Gonjarov, Sidorvuk, 1962: 5-11, 30-41).

Academician M.I. Rustamov, on the other hand, was one of the first researchers in Azerbaijan to model and optimize petroleum refining processes mathematically. He developed deterministic mathematical models for catalytic cracking processes of crude oil, fuel oil, and vacuum distillation products, solving the optimization problem of the process under non-stationary conditions and designing control schemes for its operation.

The research conducted under Academician M.I. Rustamov's direct supervision laid the foundation for theoretical and experimental studies in the field of catalytic cracking processes using finely dispersed catalysts. His works were fundamental in the development of advanced technological systems for catalytic cracking of various petroleum feedstocks, including dehydrogenation of butane to butylenes and conversion of o-xylene to phthalic anhydride.

His catalyst development for "direct flow" and "half-direct flow" lines, along with the application of various modified reactors, significantly enhanced the efficiency of reaction apparatus in catalytic cracking by 8-10 times when applied in a fluidized bed. His contributions also introduced concepts such as "activity index," "fine dispersed particles," critical flow cross-section, and the concept of "half-direct flow" to the field of technology (Rustamov, 2006).

Academician M.I. Rustamov played a leading role in the industrial implementation of significant scientific research into efficient and original petroleum refining and petrochemical processes in our republic. These processes were not only applied in our country but also extensively implemented in various cities of the former Soviet Union, as well as in Romania, Poland, and Bulgaria.

During the late 20th century, the global demand for automotive gasoline and the improvement of its quality were pressing issues, which were addressed in the scientific research of our academics, including Academician M.I. Rustamov and Professor A.J. Huseynova. Specifically, they achieved the production of AI-93 automotive gasoline through catalytic cracking processes for the first time, and industrial-type catalytic cracking units (I-B complexes) were designed and implemented at the current "Azneftyanacag" IB. (Rustamov, Aliev, Qusenova, Akimov, 1979).

Acad. M.I. Rustamov and E.M. Seyidrzayeva applied the legal compliance of various heavy (Kudron, mazut) petroleum fractions' catalytic cracking with the participation of activators and passivators. Complex schemes were developed and prepared for their industrial application (Seid-Rzaeva, Kapustin, Khansultanov, Yunis-Miax, 1990).

Furthermore, scientific research was conducted by M.I. Rustamov, G.T. Farhadova, and in the direction of destructive hydroisomerization and destructive isomerization processes aimed at obtaining small-molecule C_4-C_5 hydrocarbons. Their scientific achievements were applied using the Q-43-107 catalytic cracking complex (Rustamov, Aliev, 1980; Ismayılova, 2008: 52-56).

The development of destructive isomerization opens up new aspects of catalytic cracking. Unlike previous purposes of catalytic cracking, these processes aim not only to produce automotive gasoline but also to initiate the petroleum-chemical complex as a starting process, providing for the production of small-molecule isoparaffin and isoolefin hydrocarbons.

Patents from leading countries such as the USA, UK, France, Canada, AFR, and Japan have been obtained for the destructive hydroisomerization process involving the newly synthesized nickel-aluminosilicate catalyst (Rustamova, 2000).

Conclusion

As a result of the catalytic work conducted at the end of the 20th century, it is noteworthy to mention the surface characteristics of zeolite-based catalysts, coking, and the application of the mutual relationship between coking and its effect on the selectivity and activity of the catalytic cracking process.

The characteristics of the conducted research are such that these legal compatibilities are studied within the first seconds of contact between the catalyst and the feedstock. The results obtained allowed for the modeling of catalyst behavior throughout the reactor length and the regulation of its surface properties. This laid the scientific foundation for the creation of non-steady gasoline emulsion processes on partially coked catalysts in the catalytic cracking process, resulting in the development of the Q-43-107 catalytic cracking complex, which was then put into industrial use (Ismayılova, 2008: 126-127).

Currently, our scientists, alongside leading petroleum experts of the republic, continue work in the economically efficient direction of catalytic cracking processes, aimed at obtaining low

technological stage, perspective fuels and petrochemicals, as well as residue-free petroleum emulsions.

For instance, for the first time, with the participation of ion solutions, it has been discovered that it is possible to achieve synthetic oil composed of hybrid paraffin-naften structures that boast a high molecular weight index (HMWI) of 120 and high boil-off points (204 - 250 ^{0}C). The work, executed under the economic collaboration agreement between Azerbaijan and Ukraine, is recognized as the first project of its kind among the former USSR countries.

Moreover, for the first time, the application of the hypercritical extraction process involving CO_2 in the cleaning of asphalt-tar blends, metals and refined, heavy petroleum fractions has created a technology, processed and created in an environmentally-friendly aspect on hydrocracking (Ismayılova, 2008: 52-56).

The refined heavy petroleum and heavy petroleum fractions meet the most recent requirement and ensure the used catalysts are efficiently consumed.

References

1. Ismayilov, M. (1993). History of Azerbaijan. Azerbaijan State Publishing House. Baku. pp. 246-249.
2. Khalilov, Kh. (1990). Journey to the chemical world of Azerbaijan. Baku Science. pp. 8-45.
3. Suleymanov, M. (1989). What I heard, what I read, what I saw. Azerbaijan State Publishing House Baku. pp. 64-75.
4. Mammadaliyev, Y. H. M. (1960). Development of science in Azerbaijan. Baku. pp. 10-25.
5. Rustamov, M.I., Aliev, V. S., Gusenova, A.D. Akimov, K.A. (1979). Method for producing motor gasoline. AS (USSR) 695215 BI No. 40.
6. Seid-Rzaeva, . E. M., Kapustin, B. M., Khansultanov, R.A., Yunis-Miakh, Md. (1990). Effect of boiling control of vacuum fractions on catalytic cracking // Oil processing and petroleum. No. 3, pp. 6-8.
7. Encyclopedia of Azerbaijan. (2000). The problem of oil processing and oil chemistry in the work of academician M.I. Rustamova. Izd. Baku.
8. Rustamov, M. I., Aliev, V. S., Khudiev, A.T., Abad-zade, Kh.H., Taghiev, E. I., Veliev, T.F. (1980). Method of preparation of nickel aluminum silicate catalyst for hydrocracking and isomerization of hydrocarbons. AS No. 727213, BI No.
9. Aliev V.S., Indyukov N.M., Efimova S.A., Goncharov M.A., Sidorvuk I.I. (1962). Fluidized layer catalytic cracking. Baku. pp. 5-11, 30-41.
10. Rustamov, M.I. (2006). Catalytic process for producing high-quality motor fuels, - Baku. The science. Volume: 1-2.
11. Rustamov, M. I., Aliev, V. S., Gusenova, A. D., Akimov, K. A. (1979). Method for producing motor gasoline. AS (USSR) 695215 BI No. 40.
12. Ismayilova, Kh. Y. (2008). Development of the catalytic cracking process in oil refining. Scientific works-Fundamental sciences. No. 1, Volume: 7(25), pp. 126-127.
13. Ismayilova, Kh. Y., Gasimzadeh, E. A., Huseyinova, A. J. (2008). The role of Azerbaijani scientists in the development of the catalytic cracking process. ANT, No. 2, 2008, pp. 52-56.

Received: 18.05.2024 Accepted: 05.07.2024