



Refinery and Environment

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انتشارات ارسطو

(چاپ و نشر ایران)

۱۴۰۰

سرشناسه : محمدی ارباطی، احسان، ۱۳۷۵-

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عنوان و نام پدیدآور : Refinery and environment[Book] Ehsan Mohammadi

Arbati, Saeed Mirzaee, Seyed Mahdi Rezvan.

مشخصات نشر : ارسطو (سامانه اطلاع رسانی چاپ و نشر ایران) ، ۱۴۰۰ = ۲۰۲۲ م.

مشخصات ظاهری : ۲۰۰ ص.: مصور (بخشی رنگی)، جدول.

شابک : ۹-۸۲۸-۴۳۲-۶۰۰-۹۷۸

وضعیت فهرست نویسی : فیبا

یادداشت : انگلیسی.

آوانویسی عنوان : ریفاینری...

موضوع : نفت -- پالایشگاه‌ها -- جنبه های زیست محیطی

موضوع : Petroleum refineries -- Environmental aspects

موضوع : نفت -- پالایشگاه‌ها

موضوع : Petroleum refineries

شناسه افزوده : میرزایی، سعید، ۱۳۶۷-

شناسه افزوده : Mirzaee, Saeed, ۱۹۸۸-

شناسه افزوده : رضوان لیلان، سیدمهدی، ۱۳۷۶-

شناسه افزوده : Rezvan, Seyed Mahdi, ۱۹۹۷-

رده بندی کنگره : TP۶۹۰

رده بندی دیویی : ۶۶۵/۵۳

شماره کتابشناسی ملی : ۸۷۳۸۶۷۶

نام کتاب : Refinery and Environment

مولفان : احسان محمدی ارباطی - سعید میرزائی - سید مهدی رضوان لیلان

ناشر : ارسطو (سامانه اطلاع رسانی چاپ و نشر ایران)

تیراژ : ۱۰۰۰ جلد

نوبت چاپ : اول - ۱۴۰۰

چاپ : مدیران

قیمت : ۸۰۰۰۰ تومان

فروش نسخه الکترونیکی - کتاب رسان :

<https://chaponashr.ir/ketabresan>

شابک : ۹-۸۲۸-۴۳۲-۶۰۰-۹۷۸

تلفن مرکز پخش : ۰۹۱۲۰۲۳۹۲۵۵

www.chaponashr.ir



انتشارات ارسطو



تقدیم به

ساحت مقدس حضرت ولی عصر (عجل الله تعالی فرجه)

Preface

Humans have a responsibility to discover causes of pollution in the environment and to provide solutions to this issue. The oil and gas refinery is one of the most polluting sectors. We have written a book named *Refinery and the Environment* for the first time in the world. The primary goal of this book is to identify environmental issues created by the refinery industry and to provide effective strategies for reducing these pollutants. We drew on the findings of all researchers for this book.

Refinery and the Environment is divided into five chapters. The first chapter serves as an introduction to the subject of refinery-related environmental issues. The second chapter looks at the refinery's contribution from an environmental standpoint. The refining methods are discussed in the third chapter. This chapter also offers suggestions on how to construct ecologically friendly refinery processes. The sorts of non-fossil feed that may be utilized in the refinery are discussed in Chapter 4. Finally, in the final chapter, new materials regarding bio-refineries are written.

I'd like to thank everyone who contributed to the writing of this book, especially the energy and environmental experts who permitted their work to be included in it, as well as Mr. Behrouz Mohammadi Arbati's earnest instruction. Thank you, and in closing, I'd want to express my gratitude to our supportive parents and Mr. Mansour Mohammadi Arbati.

Contents

Introduction to Refinery and Environment.....	7
Background of the study.....	10
The Kaduna Refining and Petrochemical Company (KRPC), Kaduna	11
Problem statement	13
General objectives	14
Specific objectives.....	14
References	15
Feedstock types and properties.....	16
Introduction	16
Terminology	19
Conventional crude oil	19
High-acid crudes	21
Properties and character of naphthenic acids	21
Naphthenic acid chemistry	22
Total acid number and laboratory testing	23
Opportunity crudes	26
Foamy oil	27
Tight oil.....	28
Heavy crude oil	29
Extra heavy oil	31
Tar sand bitumen.....	32
Conventional crude oil	35
Heavy crude oil	39
Tar sand bitumen.....	39

Ultimate (elemental) composition	40
Crude oil.....	41
Distillation.....	42
Gases and naphtha.....	43
Refining processes and environment	64
Introduction	64
Refinery configurations	66
Dewatering and desalting	70
Distillation.....	71
Atmospheric distillation	73
Vacuum distillation	75
Azeotropic distillation and extractive distillation.....	76
Thermal (noncatalytic) processes	77
Thermal cracking.....	79
Visbreaking	80
Coking.....	80
Delayed coking.....	81
Fluid Coking.....	83
Catalytic cracking processes	85
Fixed-bed catalytic cracking	87
Catalysts	88
Hydroprocesses	89
Hydrotreating	89
Hydrocracking.....	91
Reforming	93
Thermal reforming	93
Catalytic reforming	95
Catalysts	97
Isomerization.....	98
Processes	98
Catalysts	99
Alkylation processes	99

Processes	100
Polymerization processes	102
Gas cleaning	107
Ancillary operations	110
The future	112
References	114
Nonfossil fuel feedstocks	116
Introduction	116
Biomass	117
Chemical constituents.....	123
Carbohydrates.....	126
Vegetable oils.....	128
Plant fibers	129
Waste.....	130
Energy crops.....	130
Cordgrass and switchgrass	137
Jerusalem artichoke	138
Miscanthus	139
Reed plants	140
Residual herbaceous biomass	141
Short-rotation coppice	142
Sorghum	142
Wood	143
History	143
Types of wood.....	146
Hardwood.....	148
Softwood	148
Composition and properties.....	148
Chemical composition.....	150
Cellulose.....	150
Hemicellulose.....	150

Lignin.....	152
Solvent-extractable materials	155
Chemistry and uses.....	157
Waste.....	162
Domestic and industrial waste.....	166
References	170
Biorefinery.....	173
Introduction	173
The biorefinery.....	176
Process options.....	180
Anaerobic digestion.....	181
Combustion	184
Fermentation and hydrolysis	186
Gasification	187
Gasifiers	188
Synthesis gas	192
Pyrolysis.....	194
Transesterification.....	195
Catalytic transesterification.....	196

Chapter 1

Introduction to Refinery and Environment

Background of the study

Nigeria is faced with rapid urbanization and industrialization, producing vast amounts of industrial wastes with little or no regulations on their handling. These industrial wastes are disposed of on arable lands and rivers (Sikder et al., 2013; Saien, 2010; Agbenin et al., 2009). Waste contributes to various toxic effects on living organisms in the food chain by bioaccumulation and biomagnification (Jadia and Fulekar, 2009). The accumulation of discharged unwanted industrial by-products released into the environment without treatment is harmful (Agarry et al., 2008; Akpan et al., 2008). Effective treatment is needed before industrial wastewaters are discharged into the environment or reused for irrigation, livestock, groundwater recharge, and other purposes (Spacil et al., 2011). Oil exploration and exploitation activities have contributed to the economic growth of Nigeria but have also resulted in several incidences of oil spills causing increased environmental pollution and degradation (Eyo-Essien, 2008). It was estimated by Kadafa (2012) that 9- 13 million barrels of oil had been spilled into the Niger Delta of Nigeria, the largest wetland in Africa, in the last 50 years, and a total range of 0.7-1.7 million tons of petroleum have been discharged into the oceans, seas, and rivers

through anthropogenic activities. Oil spills can lead to the displacement of air pore spaces in soil particles (Mustapha et al., 2015), causing vast deforestation and pollution of both water bodies and terrestrial ecosystems (Mmon and Deckor, 2010; Jadia and Fulekar, 2009; Li and Yang, 2008), eventually resulting into global environmental issues (Xia et al., 2003). Large volumes of fresh water are extracted and consumed by petroleum industries to refine crude oil and cooling agents (Saien, 2010; Shpiner et al., 2009; Allen, 2008). Similarly, large volumes of wastewater are generated (Mustapha et al., 2015). Diya'uddeen et al. (2011) reported that the produced refinery efficiency during processing amounts to 0.4 - 1.6 times the amount of crude oil processed and that this estimate is based on the yield of 13 million m³ (84 million barrels per day) of crude oil and a total of 5.3 million m³ of effluent is generated globally. Scientists and engineers have been investigating the ability of plants as remediation alternatives for treating a wide variety of pollutants in contaminated waters (Mustapha et al., 2015; Marchand et al., 2010; Jadia and Fulekar, 2009; Armfield et al., 2009). Natural treatment systems are environmentally friendly and use solar-driven biological processes to treat pollutants (Wenzel, 2009). They provide a less invasive approach than the harsh conventional methods like incineration, thermal vaporization, solvent washing, or other soil washing techniques, which can destroy the biological component of the soil or change the chemical or physical characteristics of the earth (Lin and Mendelsohn, 2009; Hinchman et al., 1996).

The Kaduna Refining and Petrochemical Company (KRPC), Kaduna

The Kaduna Refining and Petrochemical Company (KRPC) is located in Kaduna State (Nigeria). Kaduna state is situated in the Northern guinea savannah ecological zone of Nigeria. It lies between Latitude 9 ° N and 12 ° N and Longitude 6 ° E and 9 ° E of the prime meridian. The climatic condition is categorized by regular dry and wet seasons. The rains begin in April/May and end in October, while the dry season starts in late October and stops in March of the subsequent year. The mean annual rainfall is between 1450 - 2000 mm, with a mean daily temperature

regime ranging from 23 to 25° C and a relative humidity varying between 20 and 40% in January and 60 and 80% in July. It has solar radiation ranging between 20.0-25.0 Wm² days⁻¹ (Mustapha et al., 2015; Emaikwu et al., 2011).

KRPC occupies 2.89 square kilometers, approximately 15 km Southeast of Kaduna city, with roughly 615 m above mean sea level (Bako et al., 2008). It was commissioned in 1980, with an initial capacity of 100,000 Barrels per Stream Day (BPSD) as the third refinery in Nigeria to cope with the tremendous and growing demand for petroleum products (Balm et al., 2008). It has a Fuel Plant Crude Distillation Unit I (CDU I) and a Lube Plant Crude Distillation Unit II (CDU II) (Jibril et al., 2012). The Fuel Plant was designed to process 50,000 BPSD; it was later increased by an additional 60,000 BPSD bringing the total refinery installed capacity to 110,000 BPSD (Jibril et al., 2012; Bako et al., 2008). It processes Escravos light crude oil and Ughelli Quality Control Centre (UQCC) crude oil. At the same time, the Lube plant can process 50,000 BPSD of imported paraffin-rich oil to manufacture lubricating oils. The natural oils available in Nigeria cannot produce the whole range of fractions for lubricating oils, hence Nigerian National Petroleum Corporation (NNPC) imports from Venezuela, Kuwait, or Saudi Arabia (Jibril et al., 2012).



Figure 1. Google map of Kaduna refining and petrochemical company (KRPC), Kaduna. Note: S -Experimental site and R- Romi River

Problem statement

Contamination of water and lands by petroleum chemicals is a global issue. It is of particular concern in developing countries such as Nigeria, where industrial pollution is one of its significant problems. In addition, the release of untreated or partially treated petroleum refinery effluents into the environment lead to pollution of the terrestrial and aquatic ecosystems, an unaesthetic climate, high cost of wastewater treatment, loss of farmlands, fish, portable water, and means of livelihood, particularly in the oil polluted-affected community. The polluted sites are fast increasing and need to be addressed by low cost and effective technology such as constructed wetlands (CWs) (Schrlider et al., 2007). CW technology is ecologically friendly and a more economical and easier way of treating wastewater. However, the use of CWs to treat hydrocarbon contaminants in refinery wastewater and other wastewater types in Nigeria is relatively new compared to conventional treatment systems. Developing countries have largely ignored the use of CWs. CWs have been used for decades to treat different types of wastewater and have been recognized as a reliable wastewater treatment technology.

They represent a suitable solution for treating many types of wastewater (Vymazal, 2011). Therefore, there is a need to use CWs to treat petroleum-contaminated wastewater in developing nations such as Nigeria, where good water quality and resources are scarce and effective low-cost wastewater treatment strategies are critically needed. Existing technologies do not sufficiently address the increasing pollution situation. Also, most wastewater treatment plants cannot adopt some chemical approaches, such as advanced oxidation steps (Schroder et al., 2007).

General objectives

Typha latifolia and *Phragmites australis* is commonly used for petroleum wastewater treatment. Few works on treatment of petroleum contaminated wastewater have been reported on *Cyperus alternifolius* and none on *Cynodon dactylon* (L.) Pers. to the best of the author's knowledge. This study, therefore, seeks to examine the suitability of *T. latifolia*, *C. alternifolius*, *C. dactylon* and *P. australis*, for the treatment of petroleum refinery wastewater. Thus, the overall aim of this study is the polishing of secondary refinery effluent to below compliance limits recommended by regulating authorities before discharge into environment or for reuse purposes.

Specific objectives

In order to address the problems above, the following specific objectives of this research work are to:

1. Characterize the effluent from the Kaduna refining and petrochemical company (KRPC) at the point of discharged into the Romi River;
2. Design, construction, operation and monitoring of planted and unplanted VSSF, HSSF and hybrid CWs;
3. Examine the effectiveness of *T. latifolia*, *C. alternifolius* and *C. dactylon* for the treatment of petroleum-contaminated wastewater with respect to nutrient (ammonium, nitrate and phosphate), organic pollutants (BOD, COD, TPH, phenol, oil & grease) and heavy metals (Cr, Cd, Pb, Cu, Zn and Fe);

4. Examine the colonization characteristics of the microorganisms' active in the rhizosphere;
5. Determination of bioaccumulation and translocation factors of *T. latifolia*, *C. alternifolius* and *C. dactylon* and
6. Use duplex CWs planted with *P. australis* to treat petroleum contaminants (BTEX Compounds).

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Chapter 2

Feedstock types and properties

Introduction

The modern crude oil industry began in the later years of the 1850s with the discovery and subsequent commercialization of crude oil in Pennsylvania in 1859 (Bell, 1945; Yergin, 1991; Bower, 2009). The modern refining era can be said to have commenced in 1862 with the first appearance of crude oil distillation. The story of the discovery of the character of crude oil is somewhat circuitous but worthy of mention, in the historical sense (Burke, 1996).

At a time when the carbonation of water was being investigated, Joseph Priestley became involved in attempting to produce such liquid since it was to be used a cure for scurvy during the second expedition made by Captain Cook in 1771. Priestley decided to make a contribution to the success of the expedition and set himself to invent a drink that would cure scurvy. During his experiments at a brewery near his home in Leeds, he had discovered the properties of the carbon dioxide (he called it “fixed air”) given off by the fermenting beer vats. One of these properties was that when water was placed in a flat dish for a time above the vats, it acquired a pleasant, acidulous taste that reminded Priestley of seltzer mineral waters.

Experiments convinced him that the medicinal qualities of seltzer might be due to the air dissolved in it. Pouring water from one glass to another for 3 minutes in the fixed air above a beer vat achieved the same effect. By 1772 he had devised a pumping apparatus that would impregnate water with fixed air, and the system was set up on board ships *Resolution* and *Adventure* in time for the voyage by Cook. It was a great success. Meanwhile, the politics expounded by Priestley continued to dog him. His support for the French Revolution was seen as particularly traitorous, and in 1794 a mob burned down his house and laboratory. As a result, Priestley (who escaped the wrath of the mob) took ship for Pennsylvania, where he settled in Northumberland, honored by his American hosts as a major scientific figure. Then one night, while dining at Yale, he met a

young professor of chemistry. The result of their meeting would change the life of the United States in the 20th Century.

It may have been because the young man at dinner that night, Benjamin Silliman, was a hypochondriac (rather than the fact that he was a chemist) that subsequent events took the course they did. Silliman imagined that he suffered from lethargy, vertigo, nervous disorders, and whatever else he could think of. In common with other invalids, he regularly visited health spas such as Saratoga Springs, New York (at the expense of his mother), and he knew that such places were only for the rich. The meeting with Priestley apparently moved Silliman to decide to make the mineralwater cure available to the common people (also at the expense of his mother).

In 1809 Silliman set up in business with an apothecary named Darling, assembled apparatus to impregnate 50 bottles of water a day and opened two soda-water fountains in New York City, one at the Tontine Coffee House and one at the City Hotel. The decor was hugely expensive (a lot of gilt), and they only sold 70 glasses on opening day. But Darling was optimistic. A friend of Priestley visited and declared that drinking the waters would prevent yellow fever but in spite of Silliman's hopes that the business would make him rich, by the end of the summer the endeavor was a disastrous flop. It would be many more decades before the soda fountain became a cultural icon in America!

Silliman cast around for some other way to make money. Two years earlier, he had analyzed the contents of a meteor that had fallen on Weston, Connecticut, and this research had enhanced his scientific reputation. So he decided to offer his services (as a geologist) to mining companies. His degree had been in law: he was as qualified for geology as he was to be Yale professor of chemistry. The geology venture prospered, and by 1820 Silliman was in great demand for field trips, on which he took his son, Benjamin, Jr. When he retired in 1853, his son took up where he had left off, as professor of General and Applied chemistry at Yale (this time, with a degree in the subject). After writing a number of chemistry books and being elected to the National Academy of Sciences, Benjamin, Jr. took up lucrative consulting posts, as his father had done, with the Boston City Water Company and various mining enterprises.

In 1855 one of these asked him to research and report on some mineral samples from the new Pennsylvania Rock Oil Company. After several-month work, Benjamin, Jr. announced that approximately 50% of the black tar-like substance could be distilled into first-rate burning oils (which would eventually be called

kerosene and paraffin) and that an additional 40% of what was left could be distilled for other purposes, such as lubrication and gaslight. On the basis of this single report, a company was launched to finance the drilling of the Drake Well at Oil Creek, Pennsylvania, and in 1857 it became the first well to produce crude oil. It would be another 50 years before the reference by Silliman to other fractions available from the oil through extra distillation would provide gasoline for the combustion engine of the first automobile. The report by Silliman changed the world because it made possible an entirely new form of transportation and helped turn the United States into an industrial superpower.

After completion of the first well (by Edwin Drake), the surrounding areas were immediately leased and extensive drilling took place. Crude oil output in the United States increased from approximately 2000 barrels (1 barrel, bbl 542 US gallons 535 imperial gallons 55.61 ft³ 5158.8 L) in 1859 to nearly 3,000,000 bbl in 1863 and approximately 10,000,000 bbl in 1874. In 1861 the first cargo of oil, contained in wooden barrels, was sent across the Atlantic to London, and by the 1870s, refineries, tank cars, and pipelines had become characteristic features of the industry, mostly through the leadership of Standard Oil that was founded by John D. Rockefeller. Throughout the remainder of the 19th century, the United States and Russia were the two areas in which the most striking developments took place.

At the outbreak of World War I in 1914, the two major producers were the United States and Russia, but supplies of oil were also being obtained from Indonesia, Rumania, and Mexico. During the 1920s and 1930s, attention was also focused on other areas for oil production, such as the United States, the Middle East, and Indonesia. At this time, European and African countries were not considered major oil-producing areas. In the post-1945 era, Middle Eastern countries continued to rise in importance because of new discoveries of vast reserves. The United States, although continuing to be the biggest producer, was also the major consumer and thus was not a major exporter of oil. At this time, oil companies began to roam much farther in the search for oil, and significant discoveries in Europe, Africa, and Canada thus resulted.

Crude oil refining has grown increasingly complex in the last 20 years. Lower quality crude oil (such as heavy crude oil, extra heavy oil, and tar sand bitumen), crude oil price volatility, and environmental regulations that require cleaner manufacturing processes and higher performance products present new challenges to the refining industry. Improving processes and increasing the

efficiency of energy use with technology research and development are keys to meeting the challenges and maintaining the viability of the refining industry in the United States and the production of the hydrocarbon fuels upon which the modern world is dependent.

It is the purpose of this chapter to present a general description of the types of feedstocks that are currently accepted by refineries and to illustrate the evolution of the acceptance of these feedstocks from the original conventional crude oil for which the refineries were constructed.

In the simplest definition, a refinery feedstock is the crude oil produced from a reservoir (a geological formation) by means of one or more wells drilled into the formation that is destined for processing in a refinery. By this means the crude oil is transformed into one or more components and/or finished products (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017).

Terminology

Even though crude oil and its derivatives have been used for millennia, it is only in the last decade or so that some attempts have been made to standardize the nomenclature and terminology. But confusion may still exist. Therefore it is the purpose of this section to provide some semblance of order into the disordered state that exists in the segment of crude oil technology that is known as terminology.

Conventional crude oil

The term “crude oil” and the equivalent term “petroleum” cover a wide assortment of materials consisting of mixtures of hydrocarbon derivatives and other compounds containing variable amounts of sulfur, nitrogen, and oxygen, which may vary widely in volatility, specific gravity, and viscosity. Metal-containing constituents, notably those compounds that contain vanadium and nickel, usually occur in the more viscous crude oils in amounts up to several thousand parts per million and can have serious consequences during processing of these feedstocks (Speight, 2014, 2019c). Because petroleum is a mixture of widely varying constituents and proportions, its physical properties also vary widely and the color from colorless to black. Thus the definition of crude oil has been varied, unsystematic, diverse, and often archaic. Furthermore, the terminology of crude oil is a product of many years of growth. Thus the long established use of an expression, however inadequate it may be, is altered with difficulty, and a new term, however precise, is at best adopted only slowly.

Because of the need for a thorough understanding of crude oil and the associated technologies, it is essential that the definitions and the terminology of crude oil science and technology be given prime consideration. This will aid in a better understanding of crude oil, its constituents, and its various fractions. Of the many forms of terminology that have been used not all have survived, but the more commonly used are illustrated here. Particularly troublesome, and more confusing, are those terms that are applied to the more viscous materials, for example, the use of the terms bitumen and asphalt. This part of the text attempts to alleviate much of the confusion that exists, but it must be remembered that the terminology of crude oil is still open to personal choice and historical usage.

Crude oil is a mixture of gaseous, liquid, and solid hydrocarbon compounds that occur in sedimentary rock deposits throughout the world and also contains small quantities of nitrogen-containing compounds, oxygen-containing compounds, and sulfur-containing compounds as well as trace amounts of metallic constituents (Speight, 1990, 2014, 2015).

In the unrefined state, crude oil has minimal value, but when refined it provides high-value liquid fuels, solvents, lubricants, and many other products (Parkash, 2003; Gary et al., 2007; Speight, 2014, 2017; Hsu and Robinson, 2017). The fuels derived from crude oil contribute approximately one-third to one-half of the total world energy supply and are used not only for transportation fuels (i.e., gasoline, diesel fuel, and aviation fuel, among others) but also to heat buildings. Crude oil products have a wide variety of uses that vary from gaseous and liquid fuels to near-solid machinery lubricants. In addition, the residue of many refinery processes, asphalt—a once-maligned by-product—is now a premium value product for highway surfaces, roofing materials, and miscellaneous waterproofing uses.

Crude oil is a mixture of compounds boiling at different temperatures that can be separated into a variety of different generic fractions by distillation. And the terminology of these fractions has been bound by utility and often bears little relationship to composition. In fact, the molecular boundaries of crude oil cover a wide range of boiling points and carbon numbers of hydrocarbon compounds and other compounds containing nitrogen, oxygen, and sulfur, as well as metallic (porphyrin) constituents. However, the actual boundaries of such a crude oil map can only be arbitrarily defined in terms of boiling point and carbon number (Speight, 2014). In fact, crude oil is so diverse that materials from different sources exhibit different boundary limits, and for this reason