PREFACE

This book is designed to fill the need for an elementary but comprehensive account in simple terms of the principles, processes, products and equipment of a modern petroleum refinery. It has been prepared as a text book for Sarnia refinery operators participating in the recently inaugurated training courses but should prove of value to all who are interested in petroleum refining. The purposes of this text book are:

1. Definition of the technical terms used in a petroleum refinery.
2. Explanation of the fundamental principles of petroleum processing.
3. Description of the essential features of a complete refinery and of the products it produces.

The continual evolution of newer and better petroleum products, with consequent changes in established manufacturing procedures and the introduction of new processes, has reached the point where a more thorough understanding of the processes is required on the part of all operators. The first step in understanding refining processes is familiarity with the language and ideas used by chemists and engineers in developing the processes. The written and verbal descriptions of processes, equipment and products have been as a rule in terms understandable only to those with a highly technical training. This text, by explaining technical terms, attempts to bridge the gap between the technical personnel with their specialized language and the refinery operators who have had no opportunity to learn this language.

The second step in understanding refining processes is to study the underlying principles of each process and then the operating details. Study for those who have not been to school for many years may be a lost habit. However the ability to study and learn decreases, but little up to the age of 45 according to modern psychologists. Study is essentially concentration on what is said or what is read about a subject.

Effective study can be accomplished by the aid of a few simple rules.

For later edition
see the 7 January 1944
1. Concentration. When listening, listen hard. When reading, read hard. Read every word and examine every picture, graph and table of figures.

2. Writing a text book should be read in company with a pencil and a note book. After a chapter or section has been studied the gist of the subject matter should be written down in the reader's own words. Memorization of the exact words read is of little value. It is the idea behind the words that is important. Writing down the idea will be difficult but once done will be a sure part of the reader's knowledge.

3. Discussion. Discussion is a valuable form of study since it demands the expressing of ideas in words which fixes the idea in the speaker's mind, exposes his idea to the criticism of others and permits him to hear other viewpoints on the subject. Discussion is best carried out in groups of less than six where all have an opportunity to speak.

The number of correct answers to the set of self-inventory questions below will indicate a student's efficiency as a learner. These questions also indicate desirable study habits.

1. Do you study frequently for 45 minute periods?
2. Do you review a subject frequently?
3. Do you usually study every day in the same place?
4. Do you usually have a daily plan of work?
5. Do you frequently skip the graphs or tables in text books?
6. Do you frequently make simple charts or diagrams to represent points in your reading?
7. Do you write out summaries of what you have read?
8. When you find a word which you do not know, do you usually look it up in the dictionary?
9. Do you usually skim over a chapter or section before reading it in detail?
10. Do you try to memorize the text?
11. Do you frequently try to analyze your study methods to find out where you are weak?
12. Do you study at a table under good light?
13. Do you read aloud or "mouth" the words when you read?
14. Do you study with the intent of remembering?

* Taken in part from "Psychology and Life" by F.L. Ruch.
Answers of "No" to questions 5, 10, and 13 and "Yes" to the rest indicates the use of efficient study methods.

Although all the information in this text may be learned in detail, the knowledge so obtained is only an introduction to petroleum processing. The old adage "a little knowledge is a dangerous thing" is too frequently true when knowledge is not accompanied by judgment. Judgment is God-given "horse-sense" which grows with experience. Skill in operation a refinery unit depends on knowledge, judgment and experience. Time is the chief factor in the development of judgment and experience but knowledge can be obtained at a rate proportional to one's will to study, provided information is available. This text book provides at least a portion of the necessary information.

The information in this text book has been obtained in part from such publications as those of the American Society for Testing Materials, Science of Petroleum, edited by A.E. Dunston, "Petroleum Refinery Engineering" by W.H. Nelson, Imperial Oil "Lubetext" and others. For the most part, information has been obtained from members of the various departments in the Sarnia refinery. Acknowledgment for the preparation of material is made in particular to the following: Mr. N. Paterson and Mr. J. Heatley of the Process Control Department, Mr. Eric Davis of the Mechanical Department, Mr. Eric E. Lusby of the Inspection Laboratory, Mr. W. Harrison of the Instrument Department, Mr. H. Hipkin and Mr. E. Christensen. Completed sections were reviewed by Mr. H. H. Moor of the Process Control Department and Dr. J. L. Huggett of the St. Clair Processing Corporation.

G. A. Purdy.

Technical and Research Dept.
Sarnia, May 17, 1943.
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CRUDE PETROLEUM

Our modern civilization moves on a sea of oil. Gasoline from petroleum is the source of power for high speed automobile engines. High octane number aviation fuels have been instrumental in the rapid advance of aviation. Kerosene, once the chief product from crude petroleum, is still a source of illumination in many parts of the world. The advent of the streamline train, heavy duty trucks, busses, tractors and tanks have brought to the forefront the development of high speed diesel fuel oils. Furnace fuel oils for home heating have been developed. Many of our merchant ships and naval vessels depend on bunker fuel oils for steam raising. Crude petroleum is the chief source of lubricants for the industrial world. Specialized petroleum lubricants are now available for the lubrication of all types of machines from watches to 25,000 horsepower diesel engines. Today the petroleum technologist works hand in hand with the equipment design engineer, so that each new development will be assured of satisfactory and maximum performance through correct lubrication. Crude petroleum is a source of asphalts used in construction of paved highways and airports. Many types of crude petroleum yield paraffin wax. Gases from crude petroleum and the oilfields are used as domestic fuels.

In recent years the petroleum industry has entered a new phase, namely, as a source of chemicals. For many years the coal tar industry was the main source of many intermediates used in the preparation of dyes, pharmaceuticals and industrial solvents. The petroleum industry is now developing its chemical manufacturing phase. Chiefly by means of the cracking process a large variety of chemicals essential both to the war industries and the welfare of mankind are being developed from crude petroleum.

ORIGIN, GEOLOGY AND PRODUCTION OF CRUDE PETROLEUM

ORIGIN

The petroleum geologists tell us that millions of years ago the earth was a mass of dense vapor. After a time this mass gradually cooled, causing vapors to condense on the outside and ultimately forming a crust of rock. Immediately below this crust was a layer of liquid rock and below this liquid layer a space occupied by gas. A great pressure was exerted by this gas against the liquid and, in turn, against the solid crust. As this solid crust continued to cool water vapor was condensed, causing rain. This moist condition favored the growth of great masses of vegetation. Low areas in this crust were formed into lakes, rivers and oceans in which aquatic life, such as fish, oysters, etc., flourished.

As time went on changes in this crust occurred, caused by eruptions and upheavals due to the pressure of the gas finding weaknesses in the solid crust. During these upheaval periods vegetation was folded over into pockets bounded by rocks; rivers and oceans shifted and mountains were formed. These large air-free pockets containing marine life and vegetation were subjected to high temperatures and pressures, which caused
the vegetable and animal contents to decompose and undergo chemical changes. The results of these changes we know as coal, resulting from vegetation decomposition, and crude petroleum from the decomposition of organic material such as fish and other marine life. This theory, although it cannot be absolutely proved, is the most popular explanation today. The carbide theory, which was in vogue some years ago, proposing the origin of petroleum as a result of reaction between calcium bearing rock and carbon, has lost favor. The theory outlined above is substantiated by the history of the world, in which successive layers of rocks covered the earth, and it is the work of petroleum geologists (popularly called "rock hounds") to read the history of these rocks correctly and interpret them in the terms of profitable petroleum production.

GEOLGY

In the early days of oil production new fields were a mecca for fakers, who offered their services in locating oil deposits for a consideration. These fakers used an instrument known as the "divining rod", which was usually a forked hazelwood stick. While experienced operators paid little or no attention to these diviners or "oil smellers", as these unorthodox professors were commonly called, many thousands of dollars were invested by intelligent people on the basis of the affinity of the forked hazelwood stick for subterranean liquids. This forked stick is sometimes used by farmers to locate deposits of water, and instances are known where water has been found underneath the spot where the operator of this mysterious device stood with his stick, which seemingly turned without apparent effort on his part. There was a great deal of mystery connected with the diviners of oil and invariably the first requisite was payment in advance, as the smoker did not believe in a contingent fee. No record of any failures to locate oil by this means were ever preserved, only successes were remembered, and in the early days an oil operator had as much chance of striking oil by drilling a well at random as he would by following the advice of the diviner with the forked stick.

Petroleum geologists follow certain well defined procedures in their search for oil. First, oil is generally found in sedimentary rocks, such as sandstones, limestones and shales. These allow the oil to collect in the minute spaces between the particles of the rocks, much as coffee can be held by sugar that has been quickly dipped in the coffee. Another condition looked for is the existence of what is called "cap rock". This is impervious rock, which prevents the oil from escaping by seepage. The third condition looked for is a rock formation which indicates a fold or wrinkle in the earth's surface, which would allow oil to collect in a natural trap. This wrinkle or fold is often referred to as a fault. In a typical formation oil is stored in an impervious reservoir topped by cap rock. There will be a certain amount of petroleum gases present, but the bulk of the petroleum will be present as a liquid. Water present may be that trapped originally or be present due to seepage from the surface. Oil being lighter than water, yet heavier than the gas, will be sandwiched be-
between these two substances. The depth at which the oil pool lies depends largely on the shape of the various layers of earth surrounding it. Distortions, tilting and upheaval of the strata cause countless irregularities in the earth, extending deep underground. Although rivers and lakes are caused by the same distortion of the earth's surface, surface contours do not necessarily indicate the shape of structures below.

Exposed strata give the geologist a chance to estimate if oil lies below the earth's surface, but the only positive way to determine if oil is present is to drill a well. In recent years the search for crude petroleum has been greatly stimulated by highly developed scientific instruments, such as the seismograph and torsion balance. Aeroplanes have come into vogue for preliminary surveying and with the specialized instruments mentioned above, the geologist now can predict with greater certainty whether oil exists or not. However, the only positive way to decide is to drill a well.

PRODUCTION

Generally speaking there are two methods of drilling an oil well. These are by the use of cable tools (standard rig) and by rotary equipment. Cable tools employ the same principle as a pneumatic jack hammer, commonly used for breaking up concrete. The drill punches its way into the earth, crushing the rocks by force of the impact. At intervals it is necessary to remove the loosened rock, and this process is known as bailing, and the instrument, the bailer.

The rotary system of drilling, on the other hand, operates in much the same way as an ordinary brace and bit. A bit bores its way down through the earth and the loosened material is continuously brought to the surface. This is done by circulating down the pipe to which the bit is attached, a slurry of mud which emerges through the cutting bit and is forced back to the surface. In recent years rotary drilling has practically supplanted the cable tool system.

After a site has been selected by the geologist, a derrick is built to enable the driller to lift out the sections of the drilling pipe, so that he can change the bit on the end. On the derrick floor is a chain and sprocket driven turn-table, through the centre of which is vertically attached the drill pipe. This turn-table may either be steam or diesel engine driven. At the lower end of the pipe is a bit, whose type (fishtail or rock cone) depends on the formations through which it is desired to drill. As the drilling progresses and the hole becomes deeper, additional lengths must be added to the drill pipe; also, larger diameter pipe (casing) must be set in the hole to prevent surface water encroaching, to guide the drilling tools and prevent cave-ins down the hole. This casing also serves to block off pools of water that may be encountered during the drilling process. As the hole becomes deeper more casing is added, by screwing together various lengths of pipe of successively smaller diameter. As a new section of smaller diameter casing is set in the hole, a smaller diameter drilling
bit must be used, and it is common to use at least six different size diameters of casing. Removing the material broken up by the bit is done by pumping a slurry of mud down the drill pipe, and this mud also serves the purpose of blocking off water and gas, which would interfere with the drilling. As this mud comes back to the surface, bringing along the cuttings of rock, the geologist is able to determine from examination of these cuttings, what formations he is passing through. This gives him a good idea when oil may be expected. When there is a large quantity of gas existing with the oil, the oil is forced to the surface sometimes with such force that a "gusher" is formed. Unless this pressure can be brought under control the well will run wild. Frequently there is not enough gas existing with the oil to force it to the surface, and the oil must be pumped or the oil reservoir flooded with water, to bring the oil to the surface. Often it is necessary to force gas into the oil structure to bring the oil to the surface. This procedure is known as "repressuring".

When the crude petroleum comes to the surface it flows through a drum known as a separator. The gas separated here from the crude petroleum is often processed for the recovery of the light liquid hydrocarbons that it contains. Liquid hydrocarbons recovered from this gas by the processes of compression and absorption are known as casinghead gasoline. The crude petroleum from the separator generally contains water suspended in it. It is customary to reduce the quantity of water held in suspension by a process known as dehydration. This usually involves settling and a chemical or electrical treatment. After this process the oil is run to tankage and from here either pumped by means of pipe line or delivered by tanker or tank car to the refineries. When delivered by pipe line, pumping stations are spotted at intervals along the line, depending on the length of the line and the viscosity of the oil.

TYPES OF CRUDE PETROLEUM

There are many varieties of crude petroleum, some ranging from black viscous materials to light transparent products, which are green or amber in colour. For convenience sake, we will classify crude petroleum into three different groups or bases. Each base type has its definite physical and chemical characteristics, and the products obtained from each base have been found by experience to be adapted to certain definite uses. These three base types are Naphthenic base crude, Paraffinic base crude and Mixed-base crude.

NAPHTHENIC BASE CRUDE

These oils are generally found in Russia, Peru, Colombia, and certain parts of the United States, namely, California and the Texas Gulf Coast. They contain a fairly large proportion of volatile fractions, which vaporize readily. This type also contains relatively large percentages of asphalt. Generally speaking, naphthenic base crudes yield good motor and aviation fuels. In many cases they contain relatively small amounts of wax and the lubricating oils from this base type are used for what are known as low cold test oils. The kerosene obtained
from this type of crude is generally not of high quality. This type of crude is largely used for the production of aviation and motor grade gasolines, fuel oil, low cold test lubricating oils and asphalt.

**PARAFFINIC BASE CRUDE**

This type of crude petroleum occurs in the United States, principally in Pennsylvania, West Virginia and in parts of Oklahoma and Texas (Mid-Continent fields). This type is also found in Canada in the Petrolia area. The lighter fractions from this type of crude oil yield high quality kerosene, which does not smoke when ignited. They also contain relatively large quantities of crystalline and non-crystalline wax, the former being used as paraffin wax and the latter as vaseline or petrolatum. The lubricating oils from this type of crude have a comparatively constant flow rate with changing temperature and tend to resist heat, thus making them suitable for high temperature service. The gasoline produced from this type is generally of lower quality and must be further refined, to make it a good motor fuel. In general, this type of crude petroleum is used for the manufacture of kerosene, diesel fuel oils, high quality lubricants and paraffin wax.

**MIXED-BASE CRUDE PETROLEUM**

Actually no single type of crude petroleum is entirely naphthenic or paraffinic in its chemical makeup. A paraffinic base oil is predominately of that class, but also contains a small proportion of the type of compounds present in naphthenic base crude petroleum. We find in some crude petroleum, notably in Kansas, Oklahoma and Texas in the United States, and in Turner Valley in Canada, crude petroleums that contain constituents of the paraffinic and naphthenic types in such a ratio that it is impossible to classify them as either one of these two types. Consequently we have a third type of crude petroleum, which is known as Mixed-base type.

While we have pointed out the three main types of crude petroleum, it is becoming increasingly difficult to use these terms in reference to specific types of crude petroleum. It is becoming more common to classify crude petroleums as to their source. Thus we speak of Louden crude petroleum produced from fields in Louden County in the State of Illinois; West Texas and East Texas crude petroleum from various individual fields in the State of Texas. These names apply to particular fields which produce crude petroleums of relatively constant characteristics. However, even this newer type of classification is sometimes unsatisfactory, since crude petroleums of widely varied characteristics may be produced from the same field.

From the Refinery's standpoint, three factors influence the value of a crude petroleum. These are:

(a) Quality and market value of the product to be derived from the crude petroleum.

(b) The relative amounts of each product that can be obtained.

(c) The ease and amount of refinement.
All crude petroleums are not of the same quality, nor does the market value of the products which they yield command the same price; thus, naphthenic crudes, for instance, yield good motor fuels, while paraffinic crudes are important for their lubricating oil content. Due to the scarcity of crude petroleum in wartime, it is customary to pay a premium price for a particular type of crude petroleum, which gives a good yield of a certain high quality product.

Since gasoline is the largest volume product of crude petroleum, and since this volume varies from crude to crude, it is customary to pay higher prices for crude petroleums which yield high quantities of gasoline. These crude petroleums are lighter, as indicated by their gravity; crude petroleum prices are customarily based on their gravity (A.P.I. gravity). In this way the price of crude from any one field is a rough indication of its gasoline content, as the lighter gravity crude command higher prices. The third factor affecting the price of crude petroleum is determined to a large extent by the amount and kind of impurities present in it, and the ease with which these impurities can be removed. Sulphur, nitrogen and other undesirable compounds are present in all crudes in varying amounts, and when this percentage is high refining operations become expensive. It naturally follows that anything that increases refining costs reduces the margin of profit and the value of the crude petroleum to the refinery. As an example, a comparatively high gravity, high sulphur crude petroleum will command a lower price than a lower gravity, low sulphur crude petroleum. A table of assays on typical crude petroleums, giving their gravity, gasoline content and other characteristics is shown below;

<table>
<thead>
<tr>
<th>CRUDE</th>
<th>PENNSYLVANIA</th>
<th>EAST TEXAS</th>
<th>WEST TEXAS</th>
<th>COLOMBIA</th>
<th>VENEZUELA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>Paraffinic</td>
<td>Mixed</td>
<td>Mixed</td>
<td>Naphthenic</td>
<td>Naphthenic</td>
</tr>
<tr>
<td>Field</td>
<td>Bradford</td>
<td>East Texas</td>
<td>West Texas</td>
<td>La Cira</td>
<td>Lago</td>
</tr>
<tr>
<td>State</td>
<td>Pennsylvania</td>
<td>Texas</td>
<td>Texas</td>
<td>Co. S.A.</td>
<td>Ven. S.A.</td>
</tr>
<tr>
<td>Gravity, A.P.I.</td>
<td>41.5</td>
<td>38.3</td>
<td>30.6</td>
<td>26.3</td>
<td>17.8</td>
</tr>
</tbody>
</table>

NAPHTHA, 400 E.P.

| Yield Percent | 31.8 | 34.2 | 26.2 | 18.4 | 8.9 |
| Sulphur Percent | .049 | .019 | .243 | .051 | .086 |
| Oct. No. | 42. | 57. | 56. | 58.3 | 64.3 |

WATER WHITE

| Yield Percent | 12.4 | 11.8 | 9.4 | 8.2 | - |
| Sulphur Percent | .042 | .039 | .534 | .139 | - |
### LUBE DISTILLATE (NARROW CUT)

<table>
<thead>
<tr>
<th></th>
<th>17.3</th>
<th>17.3</th>
<th>16.8</th>
<th>17.3</th>
<th>10.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity @ 100 S.U.</td>
<td>131</td>
<td>177</td>
<td>236</td>
<td>375</td>
<td>193</td>
</tr>
<tr>
<td>Pour Point °F.</td>
<td>85</td>
<td>100</td>
<td>60</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Crude petroleum is essentially a mixture of liquid hydrocarbons, in which gaseous and solid hydrocarbons are dissolved. Various products are separated from crude petroleum by distillation into fractions. In order of their boiling point, the following fractions are customarily separated.

- Gases
- Straight Run Naphtha
- Water White Distillate
- Light Gas Oil
- Heavy Gas Oil
- Paraffin Distillates
- Residuum

Some of these fractions may or may not be produced, depending on the type of crude petroleum processed and the market requirements. Usually all these initial fractions will receive further treatment and in some cases be redistilled and then blended into a wide variety of finished products. As an example, straight run naphtha may be treated and added to motor gasoline or rerun to give aviation base stock or a variety of specialty solvents. Gas Oils may be further processed by cracking to yield additional quantities of naphtha, called cracked naphtha. Paraffin distillates, which are the lubricating oil fractions, receive further treatment yielding a wide variety of finished oils such as transformer, turbine, automotive and aviation oils. Wax is separated from paraffin distillate to give crystalline paraffin wax. The residue after removing paraffin distillate may be worked up into cylinder stock if a paraffinic base crude is being processed. When a naphthenic type of crude is processed the residuum, after the removal of the lubricating oil fractions, is asphalt. Mixed base crudes yield as residuum a tarry material which may be used either as asphalt or by special treatment worked up into cylinder oils.
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The rotary system of drilling, on the other hand, operates in much the same way as an ordinary brace and bit. A bit bores its way down through the earth and the loosened material is continuously brought to the surface. This is done by circulating down the pipe to which the bit is attached, a slurry of mud which emerges through the cutting bit and is forced back to the surface. In recent years rotary drilling has practically supplanted the cable tool system.

After a site has been selected by the geologist, a derrick is built to enable the driller to lift out the sections of the drilling pipe, so that he can change the bit on the end. On the derrick floor is a chain and sprocket driven turn-table, through the centre of which is vertically attached the drill pipe. This turn-table may either be steam or diesel engine driven. At the lower end of the pipe is a bit, whose type (fishtail or rock cone) depends on the formations through which it is desired to drill. As the drilling progresses and the hole becomes deeper, additional lengths must be added to the drill pipe; also, larger diameter pipe (casing) must be set in the hole to prevent surface water encroaching, to guide the drilling tools and prevent cave-ins down the hole. This casing also serves to block off pools of water that may be encountered during the drilling process. As the hole becomes deeper more casing is added, by screwing together various lengths of pipe of successively smaller diameter. As a new section of smaller diameter casing is set in the hole, a smaller diameter drilling
bit must be used, and it is common to use at least six different size diameters of casing. Removing the material broken up by the bit is done by pumping a slurry of mud down the drill pipe, and this mud also serves the purpose of blocking off water and gas, which would interfere with the drilling. As this mud comes back to the surface, bringing along the cuttings of rock, the geologist is able to determine from an examination of these cuttings, what formations he is passing through. This gives him a good idea when oil may be expected. When there is a large quantity of gas existing with the oil, the oil is forced to the surface sometimes with such force that a "gusher" is formed. Unless this pressure can be brought under control the well will run wild. Frequently there is not enough gas existing with the oil to force it to the surface, and the oil must be pumped or the oil reservoir flooded with water, to bring the oil to the surface. Often it is necessary to force gas into the oil structure to bring the oil to the surface. This procedure is known as "repressuring".

When the crude petroleum comes to the surface it flows through a drum known as a separator. The gas separated here from the crude petroleum is often processed for the recovery of the light liquid hydrocarbons that it contains. Liquid hydrocarbons recovered from this gas by the processes of compression and absorption are known as casinghead gasoline. The crude petroleum from the separator generally contains water suspended in it. It is customary to reduce the quantity of water held in suspension by a process known as dehydration. This usually involves settling and a chemical or electrical treatment. After this process the oil is run to tankage and from here either pumped by means of pipe line or delivered by tanker or tank car to the refineries. When delivered by pipe line, pumping stations are spotted at intervals along the line, depending on the length of the line and the viscosity of the oil.

**TYPES OF CRUDE PETROLEUM**

There are many varieties of crude petroleum, some ranging from black viscous materials to light transparent products, which are green or amber in colour. For convenience sake, we will classify crude petroleum into three different groups or bases. Each base type has its definite physical and chemical characteristics, and the products obtained from each base have been found by experience to be adapted to certain definite uses. These three base types are Naphthenic base crude, Paraffinic base crude and Mixed-base crude.

**NAPHTHENIC BASE CRUDE**

These oils are generally found in Russia, Peru, Colombia, and certain parts of the United States, namely, California and the Texas Gulf Coast. They contain a fairly large proportion of volatile fractions, which vaporize readily. This type also contains relatively large percentages of asphalt. Generally speaking, naphthenic base crudes yield good motor and aviation fuels. In many cases they contain relatively small amounts of wax and the lubricating oils from this base type are used for what are known as low cold test oils. The kerosene obtained
from this type of crude is generally not of high quality. This type of crude is largely used for the production of aviation and motor grade gasolines, fuel oil, low cold test lubricating oils and asphalt.

PARAFFINIC BASE CRUDE

This type of crude petroleum occurs in the United States, principally in Pennsylvania, West Virginia and in parts of Oklahoma and Texas (Mid-Continent fields). This type is also found in Canada in the Petrolia area. The lighter fractions from this type of crude oil yield high quality kerosene, which does not smoke when ignited. They also contain relatively large quantities of crystalline and non-crystalline wax, the former being used as paraffin wax and the latter as vaseline or petroleum. The lubricating oils from this type of crude have a comparatively constant flow rate with changing temperature and tend to resist heat, thus making them suitable for high temperature service. The gasoline produced from this type is generally of lower quality and must be further refined, to make it a good motor fuel. In general, this type of crude petroleum is used for the manufacture of kerosene, diesel fuel oils, high quality lubricants and paraffin wax.

MIXED-BASE CRUDE PETROLEUM

Actually no single type of crude petroleum is entirely naphthenic or paraffinic in its chemical makeup. A paraffinic base oil is predominately of that class, but also contains a small proportion of the type of compounds present in naphthenic base crude petroleum. We find in some crude petroleum, notably in Kansas, Oklahoma and Texas in the United States, and in Turner Valley in Canada, crude petroleums that contain constituents of the paraffinic and naphthenic types in such a ratio that it is impossible to classify them as either one of these two types. Consequently we have a third type of crude petroleum, which is known as Mixed-base type.

While we have pointed out the three main types of crude petroleum, it is becoming increasingly difficult to use these terms in reference to specific types of crude petroleum. It is becoming more common to classify crude petroleums as to their source. Thus we speak of Louden crude petroleum produced from fields in Louden County in the State of Illinois; West Texas and East Texas crude petroleum from various individual fields in the State of Texas. These names apply to particular fields which produce crude petroleums of relatively constant characteristics. However, even this newer type of classification is sometimes unsatisfactory, since crude petroleums of widely varied characteristics may be produced from the same field.

From the Refinery's standpoint, three factors influence the value of a crude petroleum. These are:

(a) Quality and market value of the product to be derived from the crude petroleum.

(b) The relative amounts of each product that can be obtained.

(c) The ease and amount of refinement.
All crude petroleums are not of the same quality, nor does the market value of the products which they yield command the same price; thus, naphthenic crudes, for instance, yield good motor fuels, while paraffinic crudes are important for their lubricating oil content. Due to the scarcity of crude petroleum in wartime, it is customary to pay a premium price for a particular type of crude petroleum, which gives a good yield of a certain high quality product.

Since gasoline is the largest volume product of crude petroleum, and since this volume varies from crude to crude, it is customary to pay higher prices for crude petroleums which yield high quantities of gasoline. These crude petroleums are lighter, as indicated by their gravity; crude petroleum prices are customarily based on their gravity (A.P.I. gravity). In this way the price of crude from any one field is a rough indication of its gasoline content, as the lighter gravity crudes command higher prices. The third factor affecting the price of crude petroleum is determined to a large extent by the amount and kind of impurities present in it, and the ease with which these impurities can be removed. Sulphur, nitrogen and other undesirable compounds are present in all crudes in varying amounts, and when this percentage is high refining operations become expensive. It naturally follows that anything that increases refining costs reduces the margin of profit and the value of the crude petroleum to the refinery. As an example, a comparatively high gravity, high sulphur crude petroleum will command a lower price than a lower gravity, low sulphur crude petroleum. A table of assays on typical crude petroleums, giving their gravity, gasoline content and other characteristics is shown below:

**CRUDE PETROLEUM ASSAYS**

<table>
<thead>
<tr>
<th>CRUDE</th>
<th>PENNSYLVANIA</th>
<th>EAST TEXAS</th>
<th>WEST TEXAS</th>
<th>COLOMBIA</th>
<th>VENEZUELA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>Paraffinic</td>
<td>Mixed</td>
<td>Mixed</td>
<td>Naphthenic</td>
<td>Naphthenic</td>
</tr>
<tr>
<td>Field</td>
<td>Bradford</td>
<td>East Texas</td>
<td>West Texas</td>
<td>La Cira</td>
<td>Lago</td>
</tr>
<tr>
<td>State</td>
<td>Pennsylvania</td>
<td>Texas</td>
<td>Texas</td>
<td>Co. S.A.</td>
<td>Ven. S.A.</td>
</tr>
<tr>
<td>Gravity, A.P.I.</td>
<td>41.5</td>
<td>38.3</td>
<td>30.6</td>
<td>26.3</td>
<td>17.8</td>
</tr>
</tbody>
</table>

**NAPHTHA, 400 E.P.**

<table>
<thead>
<tr>
<th></th>
<th>Yield Percent</th>
<th>Sulphur Percent</th>
<th>Oct. No.</th>
<th>WATER WHITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield Percent</td>
<td>31.8</td>
<td>.049</td>
<td>42.0</td>
<td>12.4</td>
</tr>
<tr>
<td>Sulphur Percent</td>
<td>.049</td>
<td>.019</td>
<td>.243</td>
<td>.042</td>
</tr>
<tr>
<td>Oct. No.</td>
<td>42.0</td>
<td>57.0</td>
<td>56.0</td>
<td>58.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Yield Percent</th>
<th>Sulphur Percent</th>
<th>WATER WHITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield Percent</td>
<td>11.8</td>
<td>.039</td>
<td>11.8</td>
</tr>
<tr>
<td>Sulphur Percent</td>
<td>.039</td>
<td>.534</td>
<td>.139</td>
</tr>
</tbody>
</table>
Crude petroleum is essentially a mixture of liquid hydrocarbons, in which gaseous and solid hydrocarbons are dissolved. Various products are separated from crude petroleum by distillation into fractions. In order of their boiling point, the following fractions are customarily separated.

Gases
Straight Run Naphtha
Water White Distillate
Light Gas Oil
Heavy Gas Oil
Paraffin Distillates
Residuum

Some of these fractions may or may not be produced, depending on the type of crude petroleum processed and the market requirements. Usually all these initial fractions will receive further treatment and in some cases be redistilled and then blended into a wide variety of finished products. As an example, straight run naphtha may be treated and added to motor gasoline or rerun to give aviation base stock or a variety of specialty solvents. Gas Oils may be further processed by cracking to yield additional quantities of naphtha, called cracked naphtha. Paraffin distillates, which are the lubricating oil fractions, receive further treatment yielding a wide variety of finished oils such as transformer, turbine, automotive and aviation oils. Wax is separated from paraffin distillate to give crystalline paraffin wax. The residue after removing paraffin distillate may be worked up into cylinder stock if a paraffinic base crude is being processed. When a naphthenic type of crude is processed the residuum, after the removal of the lubricating oil fractions, is asphalt. Mixed base crudes yield as residuum a tarry material which may be used either as asphalt or by special treatment worked up into cylinder oils.
REFINERY CHEMISTRY

The use of petroleum derivatives in the production of synthetic rubbers and synthetic aviation fuels has added to the refinery vocabulary terms which hitherto have remained in the chemical laboratories. In this section, new terms such as catalyst, dehydrogenase and butadiene will be explained. Some of the chemicals to be described are components of crude petroleum or of cracked petroleum. Consequently the chemistry of petroleum hydrocarbons will be discussed. Other chemicals that have been used for many years in the treating of petroleum fractions will also be described.

Basic Ideas of Chemistry

Before dealing with particular chemical terms, it is necessary to outline some of the basic ideas of chemistry.

Chemistry is concerned with the composition of substances, their various properties and the changes which substances undergo. For example, a chemist on testing table salt learns it is sodium chloride, a white crystalline solid with a specific gravity of 2.17 and a melting point of 1461°F. By experiment he learns that 35.7 parts will dissolve in 100 parts of cold water and that only 4.1 more parts will dissolve when the water is boiling. By chemical reactions he learns the changes that sodium chloride can undergo; e.g., sodium chloride on being mixed with magnesium sulphate (Epsom salts) is converted to magnesium chloride and sodium sulphate (Glauber's salt). On decomposing sodium chloride he finds it to be composed of one part of sodium, a soft, silvery metal, and one part of chlorine, a greenish, poisonous gas. In the same way, chemistry builds a knowledge of all substances.

Elements

Although sodium chloride could be decomposed into sodium and chlorine, no chemist has ever been able to decompose either sodium or chlorine into something simpler. Among the hundreds of thousands of different substances on the earth, only 94 have been found that cannot be broken down into simpler substances. These 94 substances are known as "elements". Most of the elements are rare and seldom encountered. In fact, 99% of the earth, its waters and atmosphere is made up of only 12 elements, as follows:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>49.9%</td>
</tr>
<tr>
<td>Silicon</td>
<td>26.0</td>
</tr>
<tr>
<td>Aluminum</td>
<td>7.3</td>
</tr>
<tr>
<td>Iron</td>
<td>4.1</td>
</tr>
<tr>
<td>Calcium</td>
<td>3.2%</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.3</td>
</tr>
<tr>
<td>Potassium</td>
<td>2.3</td>
</tr>
<tr>
<td>Magnesium</td>
<td>2.1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.0%</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.4</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.2</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Gold, silver, sulphur, mercury, chromium, nickel, molybdenum, nitrogen, etc., make up the remaining 1%.

Compounds

When two or more elements combine, the combination is called a "compound". For example, oxygen and hydrogen combine to form the compound water; oxygen, hydrogen and carbon combine to form the compound alcohol; oxygen and iron combine to form iron oxide (rust); sulphur and iron combine to form iron sulphide (iron pyrites or "Fools Gold").
The chemical combination of elements into a compound is not a haphazard business. A definite chemical compound always contains the same elements united in the same proportions by weight. Thus, two pounds of hydrogen unite with 16 pounds of oxygen to form 18 pounds of water. Sometimes the same elements will unite in different proportions by weight, but a different compound results. For example, if 2 pounds of hydrogen unite with 32 pounds of oxygen, hydrogen peroxide instead of water is formed.

Mixtures

Besides existing as elements or compounds, substances may be mixtures. Air, which is essentially a mixture of the gaseous elements, oxygen and nitrogen, is an example of a mixture of elements. Sand mixed with sugar is an example of a mixture of compounds.

Soil, concrete and bread are examples of mixtures of solids. Water and alcohol is a mixture of liquids; soda water is a mixture of a gas (carbon dioxide) and a liquid. Sugar dissolved in water is an example of a mixture of a solid and a liquid.

If sugar is dissolved in water, it will be noted that a relatively large volume of sugar can be dissolved in the water without changing the volume of the solution. Where did the sugar go? The explanation of this and many other chemical and physical phenomena can be made by the use of the Molecular Theory.

Molecular Theory

The molecular theory assumes that:

1. All substances are composed of tiny particles called molecules.
2. There are spaces between the molecules.
3. Molecules are always moving, even in solids.
4. There is attraction between molecules, which is very strong in the case of solids, less strong in the case of liquids, and non-existent in the case of gases.

Molecules are made up of atoms. The molecules correspond to the compounds and the atoms correspond to the elements described above. An atom may be considered as the smallest possible part of an element, while the molecule is the smallest possible part of a compound. Each element or compound is made up of its own kind of atoms or molecules. Molecules and atoms are used to describe the behaviour of individual particles of substances.

An atom is about 1/300,000,000th of an inch in diameter; consequently neither atoms nor molecules containing even thousands of atoms can be seen under the most powerful microscope. Although molecules are unimaginably small, the fact that they do exist and have the power of movement
explains how sugar disappears into water. Molecules of sugar, attracted by the water molecules, move into the spaces between the water molecules without causing the water to take up more space.

The idea of molecules also explains such things as temperature, pressure, evaporation and distillation. As mentioned above, all molecules move, even those which make up a solid. Temperature is a measure of the average speed with which they move. As heat is added, the molecules move faster and the substance becomes hotter. Gas pressure is a measure of the speed and number of the gas molecules hitting the sides of the containing vessel. Evaporation is caused by the faster molecules in a liquid breaking through the surface and escaping into the air. As explanations demand it, the idea of molecules will be used throughout this manual as an aid in explaining terms and processes.

Formulae

To show in a simple manner the combination of atoms into molecules, the atoms are designated by letters, as in the following examples:

A Hydrogen atom is denoted by H
Carbon C
Oxygen O
Sulphur S
Sodium Na
Nitrogen N

By using these letters the description of a chemical combination is shortened. Thus -

Two Hydrogen and One Oxygen react to form One Water Molecule
Atoms Atom

is shortened to

\[ 2H + O = H_2O \]

Since atoms combine to form molecules, the atoms must have points of attachment. Each kind of atom has only a limited number of points where other atoms may be joined to it. For example:

Hydrogen has 1 point of attachment \( H - \)
Carbon 4 \( - C - \)
Oxygen 2 \( - O - \)
Sulphur 6 \( - S - \)
Sodium 1 \( Na - \)

When two atoms are joined, the linkage between them (actually a chemical force) is known as a "bond" or a "valence bond". Valence bonds are shown in
structural formulae as short lines between the letters representing the atoms. Structural formulae show how the atoms in a molecule are arranged. The importance of atomic arrangement in distinguishing between different compounds containing the same number and kind of atoms (isomerism) will be discussed in the section on Hydrocarbons. Examples of formulae follow.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Ordinary Formula</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>$\text{H}_2$</td>
<td>$\text{H} - \text{H}$</td>
</tr>
<tr>
<td>Water</td>
<td>$\text{H}_2\text{O}$</td>
<td>$\text{H} - \text{O} - \text{H}$</td>
</tr>
<tr>
<td>Alcohol</td>
<td>$\text{C}_2\text{H}_5\text{OH}$</td>
<td>$\text{H} - \text{C} - \text{C} - \text{O} - \text{H}$</td>
</tr>
</tbody>
</table>

**Crude Petroleum**

Analysis of samples of crude petroleum from various oil fields would show the composition would vary, in general, as follows:

- **Mineral salts** - Traces to 10%
- **Water** - Traces to 10%
- **Sulphur** - Traces to 5%
- **Carbon** - 83 to 87%
- **Hydrogen** - 11 to 15%

The mineral salts and water are merely mixed with the crude and do not form chemical combinations with the petroleum itself. The amount of salt present is expressed as so many pounds per 1000 barrels of crude. Crudes processed at Sarnia contain about 70 pounds of salt per 1000 barrels. The mineral salts (such as sodium chloride, calcium chloride and magnesium chloride) decompose during distillation to produce with water dilute hydrochloric acid (muriatic acid) which is corrosive to the condensing equipment on the distillation units. This corrosion is overcome by the use of neutralizing chemicals and non-corrosive linings and metals.

Sulphur in crude is chemically combined with the petroleum in complex molecules. By the time the crude reaches the refinery and certainly after being heated in the stills, many of the complex sulphur compounds have broken down to produce hydrogen sulphide and mercaptans. Hydrogen sulphide ($\text{H}_2\text{S}$) is a corrosive, poisonous gas, which smells like rotten eggs. This gas is removed from petroleum fractions by washing with caustic soda solution (lye treat). The mercaptans form a series of sulphur-containing compounds with increasing boiling points. These are liquids with a very strong odour of skunk. By the lead lye treatment (Doctor Sweetening) the "sour" smelling mercaptans are converted to odourless compounds.
The carbon and hydrogen in crude are chemically combined in various arrangements into a great variety of chemical compounds. These compounds are known as "hydrocarbons". Although only the two elements, carbon and hydrogen, go into their make-up, it has been estimated there are as many as 3000 different hydrocarbons in crude petroleum. The existence of so many different hydrocarbons is due to the unique property of the carbon atoms. Unlike other kinds of atoms, carbon atoms can readily join together in almost unlimited numbers in various arrangements. Each addition of a carbon atom to a molecule and each change in the arrangement of them results in a different hydrocarbon.

Hydrocarbons with four or less carbon atoms are gaseous at ordinary temperatures and pressures. Those with five or more are liquid or solid. Some hydrocarbons contain as many as 70 carbon atoms. About three-quarters of the crude processed at Sarnia is made up of hydrocarbon molecules containing 25 or less carbon atoms.

Groups of these hydrocarbons make up the straight run fractions (naphtha, kerosene, etc.) obtained from crude. In general the names and characteristics of individual hydrocarbons in the fractions are a little concern to refinery operators.

When straight run fractions are cracked the atoms in the molecules are rearranged to produce chiefly smaller sized molecules, some of which are different from any in crude petroleum. The formation of these new ones, for example, give cracked naphtha a better octane number than straight run naphtha. The octane improving hydrocarbons will be described later on.
Section 2.

Cracking produces gases among which are "butylene" and "iso-butylene", hydrocarbons which do not exist in crude petroleum. These are the hydrocarbons required to produce Buna-S rubber polymer and Butyl rubber polymer.

The names and properties of the gases in crude, the gases produced by cracking and the liquid hydrocarbon groups that improve octane number should be part of the refinery operators knowledge.

How Hydrocarbons are Classified

The great variety of hydrocarbons, each with its own name, fortunately lends itself to a system of classification in which those hydrocarbons with similar properties are grouped together. The names and relationship of these groups are as follows:

Hydrocarbons

Saturated Hydrocarbons          Unsaturated Hydrocarbons

Paraffins         Naphthenes   Olefins          Aromatics
(Including         (Including     (Including       (Mono-olefins and)
(Isoparaffins)     (Mono-olefins) (Di-olefins.

Saturated and Unsaturated Hydrocarbons.

If all the points of attachment of the carbon atoms in a molecule are occupied by other atoms the molecule is said to be "saturated". This is illustrated by the structural formula of butane, a saturated hydrocarbon:

\[ \text{H - C - C - C - H} \]
\[ \text{H H H H} \]

However, many hydrocarbon molecules exist with some of the points of attachment not occupied by other atoms. Such hydrocarbons are called "unsaturated". This is illustrated by butylene, an unsaturated hydrocarbon:

\[ \text{H - C - C - C - H} \]
\[ \text{H H H H} \]

Note that the change from saturation to unsaturation requires the removal of two hydrogen atoms. Molecules with two hydrogens missing are called Mono-olefins. Those with four missing are called Di-olefins.

Instead of referring to the number of missing hydrogens in describing the degree of unsaturation in a molecule, the number of "double bonds"
Section 2.

is the term used. The double bond results when the ends of the bonds from which hydrogens atoms have been removed are fastened together:

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H - C - C - C - C - H} \\
\text{H H H H}
\end{array}
\]

This joining together of free valence bonds is represented in structural formulæ by the double bond as follows:

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H - C - C - C - C - H} \\
\text{H H H H}
\end{array}
\]

If two double bonds are represented, the unsaturated hydrocarbon is a di-olefin. Butadiene is an example:

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H - C - C - C - H} \\
\text{H H H H}
\end{array}
\]

Double bonds do not indicate increased chemical attraction between the two carbon atoms concerned. Rather it is a sign of weakness since unsaturated hydrocarbons will react much more readily than saturated. Showing the free valence bonds of an unsaturated molecule sticking out from their respective carbon atoms ready to attach to almost anything that comes their way, gives a better picture of the reactivity of unsaturates than the use of double bonds.

Paraffins

The paraffins form a series of saturated hydrocarbons that are characterized by their small tendency to react with other substances. The names of the hydrocarbons in this series each end in "ane". e.g., Methane. Paraffins make up a large part of most crudeoils. Paraffins with four or less carbon atoms are gases at ordinary temperatures and pressures. Crude will have dissolved in it 1 to 3% of paraffin gases (methane, ethane, propane, butane and iso-butane). Paraffins with 5 to 15 carbon atoms are liquids, which make up various proportions of straight run naphthas, kerosene and gas oils, depending on the crude from which they are distilled. Those with 16 or more are solids (waxes). Gaseous and liquid paraffins are also produced by cracking. The important paraffins are shown in the Table on page 16.

Iso-Paraffins

The first member of the paraffin series has one carbon atom and is known as methane; the second has two carbon atoms (ethane); the third has three carbon atoms (propane), and the fourth has four carbon atoms (butane). Four carbon atoms can be arranged four in a row, or three in a row with the
fourth attached to the middle atom, as follows:

\[
\begin{align*}
\text{C - C - C - C} \quad \text{or} \quad \text{C - C - C} \\
\end{align*}
\]

Both these arrangements exist, thus there are two butanes each with its own chemical and physical properties. The butane with four carbons in a row (a straight chain molecule) is called "normal butane" or simply "butane". The other butane (branched chain molecule) is called "iso-butane."

The occurrence of two or more hydrocarbons, with the same number of carbon and hydrogen atoms, is quite frequent. This is called "isomerism". For example, there are five different hydrocarbons with the formula of C₆H₁₄, as follows: (The hydrogens have been left off the structural formulae for simplification).

<table>
<thead>
<tr>
<th>Name</th>
<th>Structural Formula</th>
<th>B.P. °F</th>
<th>Gravity A.P.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Hexane</td>
<td>C-C-C-C-C-C</td>
<td>156</td>
<td>81.9</td>
</tr>
<tr>
<td>Iso-Hexane</td>
<td>C-C-C-C-C</td>
<td>157</td>
<td>77.8</td>
</tr>
<tr>
<td>(3 methyl pentane)</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iso-Hexane</td>
<td>C-C-C-C-C</td>
<td>144</td>
<td>70.4</td>
</tr>
<tr>
<td>2 methyl pentane</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iso-Hexane</td>
<td>C-C-C-C-C</td>
<td>136</td>
<td>80.3</td>
</tr>
<tr>
<td>2.2 methyl butane</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iso-Hexane</td>
<td>C-C-C-C-C</td>
<td>122</td>
<td>81.0</td>
</tr>
<tr>
<td>2.3 Methyl butane</td>
<td>C C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Naming the various iso-paraffin compounds calls for a complicated system of nomenclature, as indicated by the more specific names of the four iso-hexanes above. These names, however, need not concern the refinery operator.

Naphthenes

The naphthenes form a series of saturated hydrocarbons, in which the carbon atoms are joined in rings. The first member of this series has 3 carbon atoms joined together and is known as cyclopropane. This, and the next member of the series, cyclobutane, do not occur in petroleum. The series continues with cyclopentane, etc. This, and the heavier members of
the series, may form a considerable proportion of crude petroleum.
Naphthenes occur in both straight run and cracked naphthas and gas oils.
High boiling naphthenes predominate in lubricating oil stocks. An example
of naphthene follows:

```
H  
H  
H  
H
H

C
H

C
H

C
H
```

Cyclohexane

Olefins

Olefins do not occur in crude petroleum. They are formed when
hydrocarbons from crude are broken down or cracked. Thus the cracked gases
and cracked liquids from the cracking coils are rich in olefins—mostly
mono-olefins. Gaseous mono-olefins (ethylene, propylene, butylene and iso-
butylene) are valuable since these are the substances that can be made into
such synthetic products as alcohol, acetone, aviation blending agents and
synthetic rubbers.

Mon-olefins—usually called just olefins—differ from the par-
affins in that they have two fewer hydrogen atoms and consequently a double
bond. They form a series, the first of which is ethylene. This has two
carbon atoms. The series continues with the addition of single carbon atoms,
as in the case of paraffins. Names of members of the mon-olefin series end
in "ylene". Occasionally the ending "ene" is used. Thus "ethylene" and
"ethene" are the same thing; similarly, "butylene" and "butene" are the same.
The mon-olefins are shown in the table on page 16.

Di-olefins

The di-olefin series is similar to the mon-olefin series, except
that the members have two double bonds instead of one. These are still more
chemically reactive than the mon-olefins. This reactivity of the di-olefins is
believed to be the cause of gum formation in cracked naphtha. The di-olefins
react with one another (polymerize) to form large molecular complexes which
settle out as gum. The ease with which di-olefins polymerize is utilized in
the formation of Buna-S synthetic rubber polymer. Butadiene, a di-olefin, is
made from butylene, a mon-olefin, by removing hydrogen in a dehydrogenation
process, (Butadiene Plant). Butadiene is polymerized (with other materials)
to form Buna-S synthetic rubber polymer.

Members of the di-olefin series end in "diene". The first in the
series is propadiene; butadiene is the second and by far the most important.
Pentadiene, heptadiene, etc., occur in relatively small amounts in cracked naphthas.
The valuable butadiene occurs only as traces in refinery cracking processes,
including the Super Suspensoid cracking process. This process does produce
large quantities of butylene, which by a more severe (higher temperatures)
cracking procedure, can be converted to butadiene.
Aromatics

Aromatics are unsaturated hydrocarbons, which, like the saturated naphthenes, have their carbon atoms arranged in a ring. The first of the series is benzene. This is the basic substance, since additions of carbon atoms to the benzene ring form further members of the series. Benzene has six carbon atoms joined together. The next member, toluene, has a seventh carbon atom added as a side chain. Xylene has two carbon atoms added as two side chains on the basic six carbon ring. The structural formulae follow:

\[
\begin{align*}
\text{Benzene} & : & \text{H} \\
 & & \text{H - C - H} \\
 & & \text{H - C - H} \\
 & & \text{H - C - H} \\
\text{Toluene} & : & \text{H} \\
 & & \text{H - C - H} \\
 & & \text{H - C - H} \\
 & & \text{H - C - H} \\
\text{Xylene} & : & \text{H} \\
 & & \text{H - C - C - H} \\
 & & \text{H - C - C - H} \\
 & & \text{H - C - C - H}
\end{align*}
\]

Benzene and toluene have excellent octane numbers and do not form gum on standing. Consequently they are desired in gasolines. However, they rarely occur in crude petroleum, but are present in naphthas produced by cracking. They result from the breakdown of complex molecules which contain them. Incidentally, toluene is used to make T.N.T. (trinitrotoluene).

A review of the chief points concerning the hydrocarbon families or series is given in the table, "A Comparison of Hydrocarbon Series", on page 11. The properties of the chief hydrocarbons are given in the table, "Properties of Hydrocarbons" on page 12. Note in this table that paraffins and olefins with the same number of carbon atoms boil at similar temperatures, whereas the boiling points of compounds containing different numbers of carbon atoms per molecule are widely separated. All six hydrocarbons with 4 carbon atoms boil between 10 and 35°F. In distillation processes, these are recovered together as a group or "cut" known as the "C₄ cut". Similarly, C₂, C₃, C₅, etc. cuts are obtained.

Individual hydrocarbons are frequently given symbols which indicate the cut to which it belongs, the amount of unsaturation, if any, and if the hydrocarbon is an "iso" or "normal" compound. For example, "C₄" means a member of the C₄ cut. An "i" placed in front (iC₄) indicates it is an iso compound ("m" stands for a normal compound). A dash (-) following the symbol shows it is a mon-olefin (two dashes indicate a di-olefin). Thus the symbol iC₄- can represent only isobutylene. The symbols representing the most discussed hydrocarbons are shown in the table.
## Comparison of Hydrocarbon Series

<table>
<thead>
<tr>
<th>Paraffins</th>
<th>Naphthenes</th>
<th>Olefins</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Normal Paraffins</strong></td>
<td>Cyclohexane</td>
<td>Mono Olefins</td>
<td>Benzene</td>
</tr>
<tr>
<td>Butane</td>
<td>C₆H₁₂</td>
<td>Butylene</td>
<td>C₆H₆</td>
</tr>
<tr>
<td><strong>Iso Paraffins</strong></td>
<td></td>
<td>Butadiene</td>
<td></td>
</tr>
<tr>
<td>Isobutane</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**EXAMPLE**
- Molecular Formula: C₄H₁₀
- Structural Formula: C-C-C

**CHARACTERISTICS OF SERIES**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Chemical Reactivity</th>
<th>Bonds</th>
<th>Chief Source</th>
<th>Chief Uses</th>
<th>Name Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight Chain</td>
<td>Low</td>
<td>All single</td>
<td>Crude</td>
<td>In gasolines, kerosenes, oils, gasolines and wax.</td>
<td>end in &quot;-ane&quot; and end with &quot;-ane&quot;</td>
</tr>
<tr>
<td>Branched Chain</td>
<td>Medium</td>
<td>All single</td>
<td>Crude, cracking and synthesis</td>
<td>In high octane kerosenes, fuel oils, lube oils.</td>
<td>begin with &quot;iso&quot; and end with &quot;-ane&quot;</td>
</tr>
<tr>
<td>Ring or Branched ring</td>
<td>Low</td>
<td>All single</td>
<td>Crude</td>
<td>In gasoline, naphtha. Gaseous olefins form feed stock to polymer plants.</td>
<td>begin with &quot;cyclo-&quot; and end with &quot;-ane&quot;</td>
</tr>
<tr>
<td>Straight or Branched chain</td>
<td>High</td>
<td>One double</td>
<td>Cracking</td>
<td>Buna S rubber polymer</td>
<td>end in &quot;-yleno&quot; or &quot;-ene&quot;</td>
</tr>
<tr>
<td>Straight or Branched chain</td>
<td>Very High</td>
<td>Two double</td>
<td>Cracking and Synthesis</td>
<td>In cracked gasoline</td>
<td>end in &quot;-diene&quot;</td>
</tr>
<tr>
<td>Ring or Branched ring</td>
<td>High</td>
<td>Three or more double</td>
<td>Cracking</td>
<td></td>
<td>end in &quot;-ene&quot;</td>
</tr>
</tbody>
</table>

**Section 2.**
## Properties of Hydrocarbons

<table>
<thead>
<tr>
<th>Paraffins</th>
<th>Formula</th>
<th>Boil. Point at Atmos. °F.</th>
<th>Liquid Density at 60°F. A.P.I. lbs/bbl.</th>
<th>Vapor Pressure in p.s.i. at 100°F. (R.V.P.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 Methane</td>
<td>CH₄</td>
<td>-258.5</td>
<td>-</td>
<td>(105)</td>
</tr>
<tr>
<td>C2 Ethane</td>
<td>C₂H₆</td>
<td>-128.2</td>
<td>-</td>
<td>(138)</td>
</tr>
<tr>
<td>C₃ Propane</td>
<td>C₃H₈</td>
<td>- 43.8</td>
<td>146.5</td>
<td>178</td>
</tr>
<tr>
<td>IC₄ Iso-butane</td>
<td>C₄H₁₀</td>
<td>10.0</td>
<td>119.4</td>
<td>197</td>
</tr>
<tr>
<td>nC₄ Normal Butane</td>
<td>C₄H₁₀</td>
<td>31.1</td>
<td>110.8</td>
<td>204</td>
</tr>
<tr>
<td>Neo-pentane</td>
<td>C₅H₁₂</td>
<td>49.1</td>
<td>101.5</td>
<td>210</td>
</tr>
<tr>
<td>IC₅ Iso-pentane</td>
<td>C₅H₁₂</td>
<td>82.7</td>
<td>94.9</td>
<td>218</td>
</tr>
<tr>
<td>nC₅ Normal Pentane</td>
<td>C₅H₁₂</td>
<td>97.0</td>
<td>92.8</td>
<td>222</td>
</tr>
</tbody>
</table>

| Naphthenes | Cyclohexane | C₆H₁₂ | 176 | 50 | 273 | 3.2 |

| Olefins | C₂- Ethylene | C₂H₄ | -154.7 | - | (138) | 1340 |
|         | C₃- Propylene | C₃H₆ | - 54.0 | - | (177) | 228 |
|         | IC₄- Iso-butylene | C₄H₈ | 19.4 | 103.2 | 212 | 65 |
|         | nC₄- Butylene | C₄H₈ | 20.4 to | 98.6 to | 210 to | 45 to |
|         | Pentylenes | C₅H₁₀ | 35 | 104.3 | 214 | 65 |
|         | IC₅- Iso-pentylenes | C₅H₁₀ | 58.2 to | 81.6 to | 222 to | |

| Diolefins | C₄- Butadiene | C₄H₆ | 23.5 | 95.4 | 218 | 57 |
|           | C₅- Isoprene | C₅H₈ | 94 | 75 | 240 | 16 |

| Aromatics | Benzene | C₆H₆ | 176.2 | 28.9 | 308 | 3.2 |
|           | Styrene | C₅H₉ | 293.4 | 25.2 | 316 | 0.5 |
|           | Cumene | C₅H₁₀ | 306 | 32.7 | 301 | 0.4 |

| Miscellaneous | Hydrogen Sulphide | H₂S | - 76.5 | 47.6 | 276 | 240 |
|               | Methyl Mercaptan | CH₃SH | 43 | 31.5 | 304 | 40 |
|               | Ethyl Mercaptan | C₂H₅SH | 99 | 36.5 | 295 | 15 |
|               | Propyl Mercaptan | C₃H₇SH | 153 | - | - | 3 |
|               | Butyl Mercaptan | C₄H₉SH | 207 | - | - | 1 |
|               | Sulphuric Acid | H₂SO₄ | 617 | - | 644 | - |
|               | Girbotol (diethanolamine) | (HO CH₂CH₂)₂NH | 518 | - | 384 | - |


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REFINERY GASES

By utilizing its refinery gases, the petroleum industry has entered the field of chemical manufacture. These gases, long known to the chemist as a potential source of commercial products, are being processed into superior aviation gasolines, lubricants, synthetic rubber polymers, explosives, acetylene, anesthetics, plastics, solvents and many other chemical derivatives. In Sarnia some of the components of refinery gases will be processed to synthetic rubber polymers.

Refinery gases consist of paraffins obtained during the distillation of crude, and both olefins and paraffins obtained by cracking operations. By far the greater amount of refinery gases are produced at the cracking coils. These gases are called, in general, "cracked gases", or more specifically "high line gas." The hydrocarbon components of high line gas, arranged in cuts, are as follows:

<table>
<thead>
<tr>
<th>C₁ Cut</th>
<th>C₂ Cut</th>
<th>C₃ Cut</th>
<th>C₄ Cut</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Ethylene</td>
<td>Propylene</td>
<td>Isobutylene</td>
</tr>
<tr>
<td></td>
<td>Ethane</td>
<td>Propane</td>
<td>Butylene</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Isobutane</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Butane</td>
</tr>
</tbody>
</table>

Of these, only ethylene, isobutylene and butylene have immediate use in the production of synthetic rubber polymers. Isobutane and butane are added to motor gasoline to give it easy starting and quick pick-up qualities. The others are potential sources of various chemicals. Each of these hydrocarbons have many uses or may be converted to many different substances. The following are examples related to the rubber or petroleum industries:

Methane, as well as ethane, propane and butane, may be used in place of gasoline as a fuel for motors. The latter two are used as refrigerants. Propane may be sold as "bottled gas" in regions not served by a domestic gas distributing system. Methane, when burned to give a smoky flame, produces carbon black, an ingredient used with natural or synthetic rubber in the making of tires. Liquefied propane is used as a solvent in removing asphaltic materials, wax, etc. from lubricating oil stocks. Butane can be converted to isobutane, which is the key hydrocarbon in the making of aviation alkylate, a high octane blending agent added to aviation gasoline base stocks to increase their octane number. Any of the paraffin gases may be cracked at very high temperatures to produce olefins, including acetylene. Acetylene (HC = CH) is the first of a triple-bond series of olefins normally not produced by refinery operations. It is the starting point for the production of neoprene, a synthetic rubber, and nylon, a synthetic silk.

Ethylene and benzene produce styrene, a component of Buna-S rubber. Propylene and benzene form cumene, another aviation gasoline blending agent.

Butylenes are formed into Butyl rubber, Buna-S rubber, Vistanex, Paratac and Paratone. Paratac is added to certain greases to give them a tendency to string out. Paratone, in lubricating oils, helps prevent the oil from thinning out at high temperatures.
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Even food can be made from petroleum. Glycerine made from propylene is combined with fatty acids made from paraffin wax to form fats. These fats form a butter substitute, which the Germans consider at least better than nothing.

In general, petroleum gases are the raw materials for a host of valuable products. These gases are the potential feed stocks for dozens of new industries. An understanding of the names, properties and potentialities of refinery gases will be valuable to refinery operators now, and increasingly so in the future.

PRODUCTION OF REFINERY GASES

The gas streams in a refinery have various names, depending on where they are produced and what they contain. Gases produced at the crude distillation units and by the cracking coils contain vaporized liquid hydrocarbons (pentanes and hexanes chiefly) which will condense out as a liquid with moderate pressure and cooling. Such a mixture of vaporized liquid hydrocarbons and gases is called a "wet" gas. This mixture is also known as "light ends". When the vaporized liquids are removed by pressure, cooling, or by absorption in a light oil, the residual gas is called a "dry" gas. Since the butanes are valuable compounds, these are also recovered with the vaporized liquid components (at the Gas Absorption Plant, #2 Plant). Thus the dry gas consists essentially of methane, ethane and propane, with the corresponding olefins if they are present.

The gases obtained from the distillation of crude and from refining units at No. 1 Plant form a wet gas, which is delivered as a low pressure gas to the Gas Absorption Plant. This plant removes the butanes and heavier, which are then called absorption gasoline. The residual gas is dry gas. The gases produced by the cracking operations at No. 2 Plant form a high pressure wet gas (high line gas), which is at present processed for the recovery of butanes and heavier fractions (or Cuts) in the gas absorption plant, producing further quantities of absorption gasoline and dry gases. When production of synthetic rubber polymers begins, the high line gas will be delivered directly to the new Light Ends Recovery Unit instead of to the Gas Absorption Plant. The absorption gasoline recovered from No. 1 Plant low pressure gases will also be delivered to the Light Ends Recovery Unit.

The pressure distillate produced by the cracking coils contains a large amount of gaseous hydrocarbons due to the pressure under which it is held. These gases, and some of the liquid hydrocarbons, are fractionated out in the Debutanizer, and then re-fractionated in the Stabilizer, where the dry gases are removed overhead. The butanes and heavier (Stabilizer Bottoms) are kept in refrigerated storage to add to motor gasoline as required to increase its vapor pressure. When production of synthetic rubber polymers gets under way the light ends overhead from the Debutanizer will be delivered directly to the Light Ends Recovery Unit instead of the Stabilizer.

When the refinery is operated to produce "light ends" for the Polymer Corporation units, the debutanizer will split the pressure distillate into cracked naphtha bottoms and "light pressure distillate" overhead. In this service the Debutanizer will be known as a "Distillate Splitter".

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Ethylene, butylene and isobutylene are components in the refinery gases, which are required by the Polymer Corporation plants to produce Butyl and Buna-S rubber polymers. These gases are found in the three feed stocks delivered to the Light Ends Recovery Unit, as follows:

High Line Gas — cracked gases from the cracking coals.
Light Pressure Distillate — from the Distillate Splitter.
Absorption Gasoline — from the Gas Absorption Plant.

TREATING CHEMICALS

Crude petroleum is separated by distillation into fractions or cuts, most of which must be subjected to a chemical or physical treatment to remove various impurities. In this section, some of the more important characteristics of the chemical treating agents will be discussed. Other chemicals used in the refinery will also be covered.

1. Lye

Lye is the term used to describe the water solution of sodium hydroxide used to remove hydrogen sulphide and light mercaptans from naphtha, kerosene, gas oil, etc. Lye solution is also used to remove acidic substances, such as phenols and naphthenic acids, from gas oils and traces of sulphuric acid from acid-treated longtime-burning oil and lubricating oils.

Sodium hydroxide is also known as caustic soda. This is a white solid usually in the form of flakes, which rapidly absorb moisture from the air in sufficient amounts to turn the solid into a liquid. It is received here, however, by tank car as a solution in water. This is diluted to the desired concentration and used to wash various petroleum fractions. The lye reacts with hydrogen sulphide to form sodium sulphide, which remains in the water and thus removes the corrosive and foul-smelling hydrogen sulphide from the petroleum.

Lye, which will remove no more hydrogen or acidic compounds from petroleum products, is known as spent lye. In the spent lye obtained during the washing of gas oils there are sodium naphthenates, which have been formed by the combination of the caustic soda with naphthenic acids. By treating the spent lye with sulphuric acid the naphthenic acids can be recovered. Naphthenic acids are sold to be made into lead naphthenate, an extreme pressure agent added to lubricating oils.

Lye solutions in any concentration should not be permitted to come in contact with skin or clothing, since it will cause painful burns and destroy cloth.

2. Lead Lye Solution

Lead-lye solution, also known as Doctor Solution, is used to lead-lye treat or "Doctor sweeten" naphthas and kerosenes. This treatment removes the "sour" odour due to higher boiling mercaptans. The lead-lye solution consists of lead oxide dissolved in lye solution. The lead oxide,
also known as litharge, is a heavy reddish-yellow powder. The sodium hydroxide and the lead oxide react to form sodium plumbite. This substance converts sour-smelling heavy mercaptans to deep coloured lead mercaptides, which are soluble in petroleum. By adding a small amount of sulphur the lead mercaptide is converted to disulphides and lead sulphide. The disulphides, in contrast to the sour-smelling mercaptans, are odourless. Although they remain in the petroleum fraction, they cause no odour and thus the product is sweet. Since these disulphides have an adverse effect on the octane number characteristics of tetra-ethyl lead, they are frequently removed by redistillation from naphthas designed for gasolines. The high boiling disulphides remain in the still bottoms, which are usually sent to the cracking coils.

3. Tetra-Ethyl Lead

Gasolines of low octane number explode or detonate so fast in high compression engines that a relatively powerless blow is struck against the piston rather than a smooth powerful push. High octane gasolines produce controlled explosions, which deliver the maximum amount of power. Tetra-ethyl lead when added in small amounts to low octane gasolines, increases their octane number and thus the power obtainable from them. About 1/10th of one percent of tetra-ethyl lead will increase the octane number of gasoline from five to fifteen points, depending on the chemical characteristics of the gasoline.

Lead Tetra-ethyl itself is a heavy fluid. To this, ethyl chloride and ethyl bromide, also liquids, are added to keep any lead released during combustion in the cylinder in a volatile form. This mixture of liquids, known as ethyl fluid, is added to motor and aviation gasoline as required at the refinery.

Ethyl fluid is an exceedingly dangerous poison. Those concerned in handling it must receive special instruction and wear special clothing.

4. Inhibitors

Cracked gasolines contain olefins, chiefly mono-olefins, which have little tendency to react with one another. Di-olefins, however, have a definite tendency to polymerize into gum, particularly in the presence of heat, air and sunlight. This gum will cause a varnish-like deposit in carburetors, manifolds, and on intake valves. Certain chemicals, known as inhibitors, when added in minute traces to gasolines, prevent the diolefins from polymerizing. Inhibitors are usually complex organic compounds purchased and known by their trade name. For example, the inhibitor known as "DuPont 16" is added to cracked naphtha immediately after it is lye and water washed to prevent the di-olefins from forming gum in storage or in use.

5. Sulphuric Acid

Sulphuric acid is a heavy corrosive liquid used chiefly for the treating of lubricating oil distillates. Acid treatments are carried out in "agitators", which are tanks with cone-shaped bottoms. As a rule, 15 to 30 pounds of acid are used to treat a barrel of petroleum, depending on the type of oil. The acid reacts in many ways, as follows:
Section 2.

(a) Oxidizes and dissolves sulphur compounds.
(b) Combines with di-olefins and some mono-olefins.
(c) Polymerizes olefins.
(d) Precipitates asphalts and resins.
(e) Oxidizes mercaptans.
(f) Removes oxygen and nitrogen compounds.

After sulphuric acid is mixed with petroleum (usually by air jets) two layers form after a period of standing. The upper layer consists of oil contaminated somewhat with sulphuric acid. The lower layer, called the acid sludge, contains unchanged acid, reaction products and dissolved hydrocarbons. The acid sludge is removed through the bottom of the agitator and delivered into a cooking kettle where it is boiled with water. This separates the sludge from the dilute acid. The sludge, mixed with coal, is burned as fuel. The dilute acid is delivered to the Acid Recovery Plant. The oil remaining in the agitator is washed with water to remove the major portions of the suspended acid. It may then be given the lye wash to complete neutralization of the acid.

Sulphuric acid is used to treat Longtime Burning Oil to remove sulphur and aromatic compounds, thus removing substances which would tend to cause incrustation on the wick and a smoky flame.

Sulphuric acid is received in concentrated form (66° Be) in tank cars. This acid at any concentration will cause burns to skin and will destroy clothing. It must be handled with extreme care.

6. Clay

Two types of clay are used in a refinery; these are known as Attapulgus and Super-filtrol. Both are used to remove colour bodies, acidic compounds and unstable components from lubricating oils. After use in treating lubricating oils Super-filtrol is added to the feed stock for the Super-Suspenoid cracking operation. A certain proportion of used Attapulgus clay, and fresh Attapulgus alone, may also be used as a catalyst in the Super-Suspenoid process. Clay is contacted with lubricating oils in the Clay Contact Plant at various temperatures, depending on the type of oil. Usually this temperature is just below the flash point of the oil. While still hot the spent clay is removed from the oil by filtration in rotary filters.

The presence of clay in the cracking coil feed stock tends to scour the cracking coil tubes free of deposits of coke. By thus reducing coke formation in the tubes higher operating temperatures are obtainable which cause the formation of larger quantities of cracked gases and higher octane number hydrocarbons. After passing through the coils the clay is dropped out of the system with the cracking coil tar. The latter is filtered in the Tar Filter Plant to free it from clay. This spent clay, which is at present discarded, may be regenerated for use again.

7. Lime

Lime, also known as slake lime, is the alkaline substance calcium hydroxide. This is made into a slurry with water white and added to crude petroleum prior to distillation to react with any hydrogen chloride
formed by the decomposition of salts in the crude. Lime will also react with hydrogen sulphide. In this way the corrosive tendencies of hydrochloric acid and hydrogen sulphide are reduced.

8. Ammonia

Ammonia is a gas which is received in cylinders under sufficient pressure to maintain it as a liquid. The chief use of the gas is to create cold in the Solvent Dewaxing Plant. Heat is absorbed when liquified ammonia evaporates. Ammonia is also used to combat the corrosive action of hydrochloric acid. This acid, which is formed during the distillation of crude, attacks the cooler portions of the overhead lines and condensers. Injection of carefully controlled amounts of ammonia into the overhead lines of the crude distillation equipment counteracts the corrosive action of the acid.

9. Solvents

Various solvents are used in the refinery to separate hydrocarbons from one another.

Phenol: Phenol is a poisonous solid which melts at about 105°F. and boils at 361°F. In dilute solution phenol is known as carbolic acid. Phenol heated above its melting point and mixed in the ratio of 1 - 2 parts of phenol to 1 part of oil removes undesirable constituents from lubricating oil stocks. In the phenol treating plant the mixing of phenol and oil is brought about in the counter-current treating tower. Phenol enters the top of the tower and mixes with the raw lubricating oil, which flows upward. By this treatment, components which tend to form sludge in use and those which tend to cause the oil to thin out at elevated temperatures, are removed. The mixture of phenol and undesirable constituents, known as spent phenol, is distilled in order to recover the phenol. This can be used again. The separated undesirable constituents, known as phenol extract, is used as bunker fuel oil. Phenol in the treated oil is also recovered by distillation.

Ketone: Waxy lubricating oil distillates are dewaxed in the solvent dewaxing plant by means of a mixture of solvents, whose chemical names are normal propyl ketone and normal butyl ketone, more commonly referred to as simply ketone. When a solution of lubricating oil distillate and ketone is chilled to temperatures approaching 0°F., the ketone has the property of retaining the lubricating oil portion of the distillate in solution, while the wax remains undissolved. The wax is then separated by filtration and the ketone distilled from the lubricating oil. The ketone may then be used again. Although ketone is a non-poisonous substance, its vapors, however, will form an explosive mixture.

Other solvents are used in the production of synthetic rubber polymers. Sulphuric acid, acetone and cuprous ammonium acetate, are used as solvents in the various processes concerned.

10. Aluminum Oxide (or alumina)

Aluminum oxide in red crystal form is known as ruby, in blue crystals as sapphires. Aluminum oxide is also known in other forms as corundum and emery. Alundum, an artificial abrasive, is also aluminum oxide.
In the form of a white powder it has the property of absorbing moisture from gases and liquids. Aluminum oxide will be used for this purpose in drying the feed stocks to the various synthetic rubber polymer plants.

11. Girbotol (di-ethanol-amine)

This is an organic liquid which will absorb hydrogen sulphide from refinery gases. The hydrogen sulphide can be removed from the di-ethanol-amine by heat and used to absorb more hydrogen sulphide. This is the process which will remove hydrogen sulphide from the gaseous feed to the new Light Ends Recovery Unit.

12. Cumene

Cumene is a high octane number blending agent, which is added to aviation gasoline base stocks to increase their octane number. It will be made at #2 Plant from benzene and propylene by high temperatures and a phosphoric acid catalyst. Former low pressure cracking coils are being converted for this new purpose.

CHEMICAL TERMS

1. Polymerization

The joining together of hundreds or thousands of like molecules into a single complex large molecule is called polymerization. This term also describes the plant operation of converting gaseous hydrocarbons to synthetic rubber polymers. For example, butadiene is polymerized with styrene into Buna-S rubber polymer. Polymerization also describes the formation of gum in uninhibited cracked naphtha by the joining together of diolefins. In each case the product of polymerization is properly called a "polymer". Synthetic rubber polymers are converted to synthetic rubber by the addition of other substances, (i.e.; carbon black) and by vulcanization.

2. Dehydrogenation

When atoms of hydrogen are removed from a molecule, usually by heat in the presence of a catalyst, the process is called dehydrogenation. This process will take place in the new Butadiene Unit, where hydrogen will be removed from butylene to produce butadiene. It will also be used in the Styrene Plant to convert ethyl benzene to styrene.

3. Isomerization

The conversion of normal butane to isobutane is called Isomerization. Normal butane, which is relatively plentiful in a refinery, is inert in the reaction which forms aviation alkylate. Isobutane, which is relatively scarce in the refinery, is required for the reaction; hence the development of this process to convert normal butane into isobutane.

4. Alkylation

The combination of isobutane with an olefin (ethylene, propylene, butylene, isobutylene or pentylene) to form a high octane isoparaffinic liquid is known as alkylation. The isoparaffinic liquid, aviation alkylate, is added to aviation gasoline base stocks to produce higher octane numbers.
5. Catalyst

A catalyst is any foreign substance which, by its mere presence, causes a chemical reaction to take place or directs it in the desired direction. Clay in the cracking coil feed stock not only scourrs the tubes free of coke, but may direct the chemical reactions taking place in the cracking coils to produce more isoparaffinic and aromatic compounds at the expense of the undesired paraffinic compounds. Catalysts are required for several of the chemical reactions required for the production of synthetic rubber polymers. For example, aluminum chloride causes ethylene and benzene to combine to form ethyl-benzene. By an alumina-type catalyst (aluminum oxide) ethyl-benzene is converted to styrene, one of the components of Buna-S rubber. Butadiene, the other chief component of Buna-S rubber, is made from butylene by the use of still another catalyst.

Sulphuric acid acts as a catalyst in the formation of aviation alkylate from gaseous olefins and iso-butane. Aviation alkylate is a synthetic liquid hydrocarbon consisting to a large extent of iso-octane (an isoparaffin) which is added to aviation gasoline base stocks to increase their number.

Phosphoric acid is the catalyst used in the production of cumene from propylene and benzene. Phosphoric acid is a syrup liquid. When used as a catalyst, it is impregnated on pellets of an inert material such as Kieselguhr. In this way, the catalyst is spread out in order to contact the gaseous propylene and benzene passing through the catalyst bed.
PHYSICAL PRINCIPLES

Substances may be changed by chemical means. These changes are permanent changes caused by removing, rearranging or substituting atoms in the molecules of the substance. Substances may also be changed by physical means. These changes do not involve the atoms of the molecules – only the state of the molecules. For example, when water is heated through its boiling temperature, the water molecules change from the liquid state to the gaseous state (steam). The atoms in the water molecule, in both the liquid and gaseous states, are unaffected. On cooling the steam, the same water is obtained. Physical changes underly most of the refining carried out in a petroleum refinery. Distillation, evaporation, extraction, solution, melting, solidification, condensation, etc., are all physical changes. A refinery operator cannot know too much concerning the mechanics and laws of physical change.

States of Matter

All substances exist in one of the three states of matter: solid, liquid or gas. The state attributed to a substance is the one that is most familiar. For example, iron is considered a solid, water a liquid and air a gas. Changes in temperature will convert any of these to the other states. By adding heat to iron it becomes a liquid, molten iron; on adding more heat until a temperature of about 4420°F is reached, the molten iron boils and changes to vapor (gas). Even air can be changed to the liquid and solid states by extreme cooling and pressure.

Since by far the largest part of the products produced by a refinery are liquids, and these are refined for the most part by changes in state from liquid to vapor and back again (distillation), attention will be directed to these states in particular.

MOLECULAR MECHANICS

Molecules and Matter

The behaviour of liquids and gases under various conditions of temperature, pressure, etc., can be visualized in general if the idea of molecules is kept in mind. Molecules are exceedingly small particles of matter. They may be imagined as tiny balls. Each molecule is separated from its neighbour. In solids the space between molecules is small, in liquids somewhat greater and in gases very great. Molecules have an attraction for one another, except in the gaseous state. In solids this attraction is so great that the molecules cannot move past one another, and since the space between molecules is very small their motion is simply a limited vibration. Furthermore, the attraction between molecules in a solid is strong enough to give the bulk of the substance a rigid form. In liquids the attraction between molecules is not sufficient to cause rigidity, but it is still strong enough to hold the molecules together, although they can move past one another. In gases the attraction between molecules is non-existent. The molecules have no tendency to hang together at all - they will separate as far apart as the walls of the containing vessel will permit. If there are no walls, the gas molecules will continue to separate from one another indefinitely. In gases, the actual volume of the molecules is insignificant compared with the space occupied.
Section 3.

Molecules and Temperature

All molecules in gases, liquids and even in solids are in perpetual motion. In liquids and solids the motion may be imagined as a short to and fro motion, limited by the relatively strong attraction between molecules. Molecules in motion give a mechanical picture of temperature; the faster that molecules move the higher the temperature. Heat added to a gas, liquid or solid causes the molecules to speed up. This increase in speed shows up as an increase in temperature. The molecules may be imagined hitting the bulb of a thermometer; the faster they go, the harder they hit, and the farther they drive the mercury up the thermometer. Molecules, despite their small size, have an appreciable striking force, since they travel at rates well over a 1000 miles per hour.

Heat added to petroleum as it passes through a pipe still causes petroleum molecules to move or vibrate faster. In this way energy is added to the petroleum, which is used in the bubble tower to separate the petroleum into fractions. This energy causes the lightest fractions to move the fastest, and the heavy fractions to move the slowest. The high-speed, hard to stop, molecules of the light fractions leave the top of the tower as a gas. The slower, intermediate fractions are sufficiently slowed down in the tower to cause them to condense. These are drawn off as liquid side streams. The heavy fractions (bottoms) have molecules so large that the heat has speeded them up very little despite the fact that they are at high temperatures. Consequently they make little attempt to go up the tower at all. The idea of molecular speed being related to the size of the molecule will be important when distillation is described.

Molecules and Pressure

Solids and liquids are almost incompressible, or in other words, pressure exerted on liquids and solids will cause them to contract in size very little. The attraction between the molecules of solids and liquids is relatively so great that any ordinary pressure applied to them will not increase these attractive forces sufficiently to pack the molecules closer together.

Gases are compressible; the addition of pressure causes gases to contract and removing pressure causes them to expand. Since there is no attractive force between gaseous molecules, any added pressure causes them to pack closer together.

Gases create pressure due to the motion of their molecules. If the molecules are visualized as tiny bullets travelling at 1000 to 4000 miles per hour, striking the walls of the containing vessel, the idea of pressure can be readily understood. The molecules, millions per second, strike the walls, bounce off to strike other molecules or a wall on another side. This process goes on without cease. If the gas is cooled, the molecules slow down and the pressure thus drops. If the gas is crowded into a smaller space, such as happens when a piston compresses gas in a cylinder, the molecules have shorter distances to travel to hit the walls and thus hit them more frequently with a corresponding increase in pressure.
Thermal Changes

It is a matter of common experience that matter passes from solid to liquid and finally to the gaseous state on heating. Heat is a form of energy which, when imparted to molecules, increase their energy and hence the amount of movement. Temperature is a measure of this amount of movement and can be directly related to the energy of the molecules. The method of measuring quantity of heat used in industry is to take as a standard or unit the amount of heat required to raise the temperature of 1 lb. of water 1°F. This quantity of heat is called the British Thermal Unit (B.T.U.).

In a substance containing no heat, that is, no thermal energy, molecules are motionless and fixed in position; an extremely low temperature is needed to attain this state and is called "absolute zero". On the Fahrenheit scale this is 460°F below zero and on the Centigrade scale 273° below zero. When the temperature is raised by adding heat to the substance, the molecules acquire increasing amounts of vibration, which has the effect of causing the solid to expand slightly. Finally the vibration becomes so violent that the molecules shake themselves free from their fixed positions and begin to move past each other; the temperature at which this change occurs is called the melting point. Molecular movement continues to increase as more heat is added and the liquid similarly increases in volume. A proportion of the molecules will, by collision with others, acquire higher speeds than the average and some of the particularly fast-moving ones will have sufficient energy to break away entirely from the forces of attraction and enter the space above the liquid. If the liquid is in a large closed container, the number of molecules in the gas will continue to increase until the number leaving the liquid is just equal to the number of molecules returning from the gas space into the liquid. At this point the gas is said to be in equilibrium with the liquid. The molecules in the gas space will be continually rebounding from the walls of the container, and this bombardment will result in a uniform force on each wall of the vessel. This force is usually called the pressure of the gas. The pressure is determined by the number of molecules in the gas and their velocities, which in turn are both determined by the temperature of the liquid, at a given temperature, therefore, each liquid will exert a definite vapor pressure. In the graph on page 4 is shown the variation of the vapor pressure of water with temperature. A convenient measure of the volatility of a substance is the vapor pressure it will exert at 100°F expressed as pounds per square inch. In the petroleum industry, this quantity is measured in a Reid Vapor Pressure apparatus and is called the Reid Vapor Pressure (R.V.P.).

As more heat is added to the liquid in the container mentioned above, more molecules escape into the vapor space above the liquid. Furthermore, the speed of the molecules in the vapor space increases due to the heat. Accordingly, the pressure will increase rapidly until all the liquid is vaporized. Further increase in temperature will then only increase molecular speeds, but will not affect the number of molecules in the gas space; consequently the pressure will rise at a much slower rate than when liquid was present.

If instead of being enclosed in a container, the liquid is placed in a vessel exposed to the air, the molecules leaving the liquid usually have no chance of returning. This process is called evaporation. This involves
continual removal of the fast-moving molecules from the liquid. Since only slow-moving ones are left behind, it follows that the temperature of the liquid will fall unless heat is supplied from outside. This cooling effect is more evident when volatile substances, such as ammonia liquified by pressure at room temperature is released through a valve to the atmosphere. This is put to practical use in many refrigeration units.

SOLIDS

Since the solid materials in a refinery are, for the most part, brick concrete, steel, etc., the properties of solids are primarily the concern of those concerned with the design and construction of process equipment. However, the process operator should have a general knowledge of the effect of temperature, pressure, etc., on the materials out of which his unit is made.

Density of Solids

In general, solids are the heaviest of all materials. The idea of heaviness is expressed by the term "density". Density is the mass of a unit volume of the substance. In the English system of measurement, the mass is expressed as pounds and the unit volume is one cubic foot. For example, the
density of a cubic foot of iron is 462.5 lbs; the density of a cubic foot of aluminum is 165.6 lbs., and a cubic foot of cork has a density of 15.6 lbs. Each solid has its characteristic density. If the density and volume of a large object is known, its weight can be calculated by multiplying the volume by the density.

Specific Gravity of Solids

Specific gravity is a term which describes the ratio between the density of some substance and the density of water; in other words, the ratio of the weight of a cubic foot of some substance to the weight of a cubic foot of water. A cubic foot of water weights 62.38 lbs.; a cubic foot of iron weights 462.5 lbs. The specific gravity of iron is 462.5 divided by 62.38, which equals 7.4. This means that iron is 7.4 times heavier than water. From the weight of a piece of solid of any convenient size, and the weight of the water which this piece of solid displaces, the specific gravity can be determined. By multiplying the specific gravity by the weight of a cubic foot of water, the density of the solid in pounds per cubic foot is obtained.

\[
\frac{\text{Wt. of Solid}}{\text{Wt. of equal Volume of Water}} = \text{Specific Gravity}
\]

\[
\text{Specific Gravity} \times 62.38 = \text{Density of Solid in lbs/cu. ft.}
\]

Expansion and Contraction of Solids

All solids expand when heated. For the same temperature change each solid expands a different amount. For example, a bar of iron 10 feet long heated from 60°F. to 100°F. will lengthen 1/32" more than a similar bar of brass. The fraction of its own length that a bar or tube of metal will expand for each increase of 1°F. is known as the coefficient of linear expansion. These coefficients for some of the materials used in the refinery are as follows:

<table>
<thead>
<tr>
<th>Material</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>0.0000161</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.0000123</td>
</tr>
<tr>
<td>Brass</td>
<td>0.0000104</td>
</tr>
<tr>
<td>Iron and Steel</td>
<td>0.0000063</td>
</tr>
<tr>
<td>Brick</td>
<td>0.0000031</td>
</tr>
<tr>
<td>Concrete</td>
<td>0.0000008</td>
</tr>
</tbody>
</table>

A 10-ft. bar of lead would increase in length on being heated from 60°F. to 100°F.:

\[
10' \times 12'' \times (100 - 60°F.) \times 0.0000161 = 0.077 \text{ inches} = \frac{77}{1000} = 1/13 \text{ inches.}
\]
Strength of Solids

The strength of a solid depends on the material from which it is made, and in many cases, on the temperature. The strength of various materials is usually expressed as the weight in pounds required to pull apart a 1" square bar of the material. This is called the tensile strength. The tensile strength of various substances at room temperature are as follows:

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass</td>
<td>26,880 #/sq. in.</td>
</tr>
<tr>
<td>Copper - Cast</td>
<td>22,450</td>
</tr>
<tr>
<td>Sheet</td>
<td>30,240</td>
</tr>
<tr>
<td>Wire</td>
<td>40,000</td>
</tr>
<tr>
<td>Steel - Cast</td>
<td>80,000</td>
</tr>
<tr>
<td>Forged</td>
<td>95,000</td>
</tr>
<tr>
<td>Wood</td>
<td>10,000 to 20,000</td>
</tr>
</tbody>
</table>

The tensile strength of metals is dependent on their temperature. Ordinary steel has practically the same strength up to about 700°F. At temperatures above this its strength is progressively reduced. High temperature strength is obtained by the use of extra thicknesses of steel, or by the use of special alloys. Tubes for tube still furnaces, in which oil is heated to temperatures over 1000°F., are usually made of an alloy of steel with 5% chromium and 1/2% molybdenum.

Elasticity

All metals are elastic to a certain extent. Lead, for example, has a negligible elasticity, while spring steel has a relatively great elasticity. Elasticity is the ability of a material to recover its original size and shape after being stretched or bent out of shape. However, metals may be bent or stretched only so far and still retain their original size and shape when released. If they are stretched beyond this point, known as the elastic limit, the metal will be permanently deformed. Furthermore, its tensile strength will be greatly reduced. If a pressure vessel is subjected to sufficient pressure to stretch the steel beyond its elastic limit, the walls of the vessel will be so weakened that they will give away when subjected subsequently to much lower pressures. Safety valves, however, prevent accidents due to exceeding the elastic limit. Safety valves are usually set to open at not more than one-quarter of the maximum pressure the steel is calculated to hold.

Corrosion

All metals are subject to corrosion, but not all are corroded by the same materials or conditions. For example, ordinary steel will rust in contact with air and moisture, while stainless steel, an alloy of iron and chromium, will remain unharmed. Hydrochloric acid, which is usually formed in the distillation of crude, will attack both ordinary and stainless steel, but has
little effect on admiralty metal, a form of brass. The subject of corrosion and its control is discussed in the section on "Corrosion and its Control".

LIQUIDS

Since the products produced in the refinery are chiefly liquids, and since great volumes of water are used in condensers and coolers and to make steam, the properties of liquids are of particular concern to the refinery operator.

Viscosity of Liquids

The property which differentiates a liquid from a solid is the ability of the former to flow. The rate with which a liquid flows depends on the kind of liquid and its temperature. Some liquids, such as pitch or molasses, which flow with difficulty, are "viscous"; others, such as water and naphtha, which flow readily, are "mobile". The ability of a liquid to flow is determined by the resistance that one layer of liquid experiences in sliding over another (internal friction). This resistance to flow, due to resistance within the liquid itself, is called "viscosity". Cold liquids frequently have a high viscosity (viscous liquid); on heating these liquids, their viscosity decreases and in many cases the liquid becomes very mobile.

Viscosity is important to the petroleum industry, since this is one of the chief characteristics of lubricating oils. The viscosity of lubricating oils is measured by finding the time in seconds required for 60 millilitres of oil at a definite temperature to flow through a certain sized hole in the bottom of a laboratory test apparatus called the Saybolt Viscosimeter. If the hole is the smaller of the two sizes used, the viscosity of the oil is reported as so many seconds at the specified temperature "Saybolt Universal". For example, 35 seconds @ 100°F. S.U. If the larger hole is used the oil flows 10 times faster and the results are reported as "Saybolt Furol" (S.F.).

Volume of Liquids

Petroleum is measured by the barrel and by the gallon. The barrel used by the petroleum industry is a special size that contains 42 wine or U.S. gallons (35 Imperial Gallons). The U.S. gallon is 0.8327 (about 5/6) of an Imperial gallon. Refinery operations are measured in terms of barrels and U.S. gallons, while sales of finished products are made in Canada on the basis of the Imperial gallon.

Very small quantities, such as required in laboratory tests, are measured in "millilitres" (m.l.), also called "cubic centimetres" (c.c.). A millilitre or cubic centimetre of water weighs one "gram". A ten cent piece weighs about 2.3 grams. There are 3785 m.l. (or c.c.) in one U.S. gallon.

Density of Liquids

As in the case of solids, liquids also have density. For example, a cubic foot of water has a density of 62.38 lbs. and kerosene has a density
of 50 lbs. The density of liquids and solids, however, is not of particular
importance to the refinery operator. The specific gravity of liquids, and
particularly the "A.P.I. gravity", are important.

Specific Gravity of Liquids

The specific gravity of a liquid is the ratio of the weight of a
definite volume to the liquid and the weight of an equal volume of water,
both at some definite temperature. The specific gravity of kerosene, for
example, may be found by dividing the weight of a cubic foot of kerosene
(50#) by the weight of a cubic foot of water (62.38#) when both are at 60°F.
This equals 0.8, the specific gravity of kerosene. Sulphuric acid, which
weighs 125# per cu. ft. would have a specific gravity of 1.84.

Specific gravity is usually determined by means of a hydrometer.
This is a glass tube of a definite weight and volume, which can be floated
in the liquid whose specific gravity is desired. Within the tube is a scale,
such that when it is floated in water at 60°F the number "1" appears just
at the surface of the water. In liquids lighter than water (or in water at
temperatures over 60°F) the tube sinks a certain amount, showing a number
less than 1 at the surface of the liquid. For example, the hydrometer in
kerosene would float at 0.8. Conversely, in liquids heavier than water (or
water colder than 60°F) the hydrometer floats higher where a number greater
than 1 is at the surface of the liquid. For example, in sulphuric acid the
liquid level would be at 1.84. Specific gravities of liquids will range
from about 0.5 to 2.0.

Baume Gravity

Since this scale is relatively small, other scales have been develop-
ed to give a wider range of numbers. Baume invented a scale with a value of
1 for water and a 10% salt solution having a value of 10. In this case, the
gravity of liquids heavier than water is expressed in a range from 0 to about
75, instead of from 1 to 2, as in the case of specific gravity. These numbers
are called degrees and are represented by the symbol "°Be". This scale is little
used in the refinery except to express the concentration of lye solutions and
the concentration of sulphuric acid.

In the following table the first line shows the concentration, Baume
gravity and specific gravity of lye solution (sodium hydroxide, NaOH, in water)
and sulphuric acid, H₂SO₄, as received at the refinery. The following lines
show the values of these quantities as water is added.

<table>
<thead>
<tr>
<th>Lye Solution</th>
<th>Sulphuric Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>% NaOH</td>
<td>°Be</td>
</tr>
<tr>
<td>50</td>
<td>49.9</td>
</tr>
<tr>
<td>40</td>
<td>43.6</td>
</tr>
<tr>
<td>30</td>
<td>35.8</td>
</tr>
<tr>
<td>20</td>
<td>26.1</td>
</tr>
<tr>
<td>15</td>
<td>20.4</td>
</tr>
<tr>
<td>10</td>
<td>14.2</td>
</tr>
<tr>
<td>5</td>
<td>7.4</td>
</tr>
<tr>
<td>1</td>
<td>1.4</td>
</tr>
</tbody>
</table>