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ALTERNATE FEEDSTOCKS IN THE REFINERY

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Abstract: Over the past four decades, the energy industry has experienced significant changes in resource availability, petro-politics, and technological advancements dictated by the changing quality of refinery feedstock. However, the dependence to fossil fuels as primary energy source has remained unchanged. Advancements made in exploration, production, and refining technologies allow utilization of resources that might have been considered unsuitable in the middle decades of the 20th Century. As the 21st Century opened, the refining industry entered a significant transition period and the continued reassessment by various governments, and the various levels of government, of oil importing policies and oil exporting policies. Therefore, it is not surprising that refinery operations have evolved to include a range of next-generation processes as the demand for transportation fuels and fuel oil has shown a steady growth. A major challenge is the feedstock composition because of the high content of heteroatoms (sulfur, nitrogen, oxygen) and heavy metals (particularly nickel and vanadium) and the high propensity for coke formation which is accompanied by a decrease in the yield of distillates. In addition, the evolution of refinery processing to the use of alternate (non-fossil fuel) feedstocks is also presented in anticipation of domestic and industrial waste into the refinery for blending into conventional (fossil fuel) feedstocks or for separate processing. Many refineries may have already begun such planning by incorporating a gasifier on the refinery site. This will lead to the production of gaseous products, especially synthesis gas – a mixture of carbon monoxide and hydrogen – that can, through the Fisher-Tropsch process, give rise to a variety of products. By understanding the evolutionary changes that have occurred to date, coupled with a presentation of possible future scenarios, this presentation will satisfy the needs of engineers and scientists at all levels from academia to the refinery and help in understanding the refining and prepare for the new changes and evolution of the industry.
Keywords: Refinery configuration, biorefinery, gasification refinery, Fischer-Tropsch synthesis, alternate feedstocks, reconfigured refinery

INTRODUCTION

To meet the challenges from the changing tends in current feedstocks into a refinery to changes in the feedstock composition and also to changes in the product slate, the refinery will adapt to produce the ultimate amounts liquid fuels from the feedstock and maintain emissions within environmental compliance [1, 2, 3]. A major trend in the refining industry market demand for refined products will be in synthesizing fuels from simple basic reactants (such as synthesis gas) when it becomes uneconomical to produce super clean transportation fuels through conventional refining processes. Fischer-Tropsch plants together with IGCC systems will be integrated with or even into refineries, which will offer the advantage of high quality products [4].

This paper presents suggestions and opinions of the means by which refinery processes will evolve during the next three-to-five decades. Material relevant to (i) comparisons of current conventional feedstocks with viscous feedstocks and bio-feedstocks, (ii) the evolution of refineries since the 1950s, (iii) the properties and refinability of viscous feedstocks and bio-feedstocks, (iv) the choice between thermal processes and hydroprocesses, and (v) the evolution of products to match the environmental market.

REFINERY CONFIGURATION

Refineries need to be constantly adapted and upgraded to remain viable and responsive to ever changing patterns of crude supply and product market demands. As a result, refineries have been introducing increasingly complex and expensive processes to gain higher yields of lower boiling products from the higher boiling fractions and residua [5, 6]. Finally, the yields and quality of refined crude oil products produced by any given oil refinery depends on the mixture of crude oil used as feedstock and the configuration of the refinery facilities. Light/sweet crude oil is generally more expensive and has inherent great yields of higher value low boiling products such naphtha, gasoline, jet fuel, kerosene, and diesel fuel. Viscous sour (high sulfur) feedstocks are generally less expensive and produces greater yields of lower value higher boiling products that must be converted into lower boiling products.

— Crude Oil Refinery

A crude oil refinery is an industrial processing plant that is collection of integrated process units (Figure 1). The crude oil feedstock is typically a blend of two or more crude oils, often with viscous feedstocks blended in compatible amounts. With the depletion of known crude oil reserves, refining companies are having to seek crude oil in places other than the usual sources of supply.

The definition of refinery feedstocks is often confusing and variable and has been made even confusing by the introduction of other terms that add little, if anything to crude oil definitions and terminology [3, 5, 6]. The configuration of refineries may vary from refinery to refinery. Some refineries may be more oriented toward the production of gasoline (large reforming and/or catalytic cracking) whereas the configuration of other refineries may be more oriented towards the production of middle distillates such as jet fuel, and gas oil.

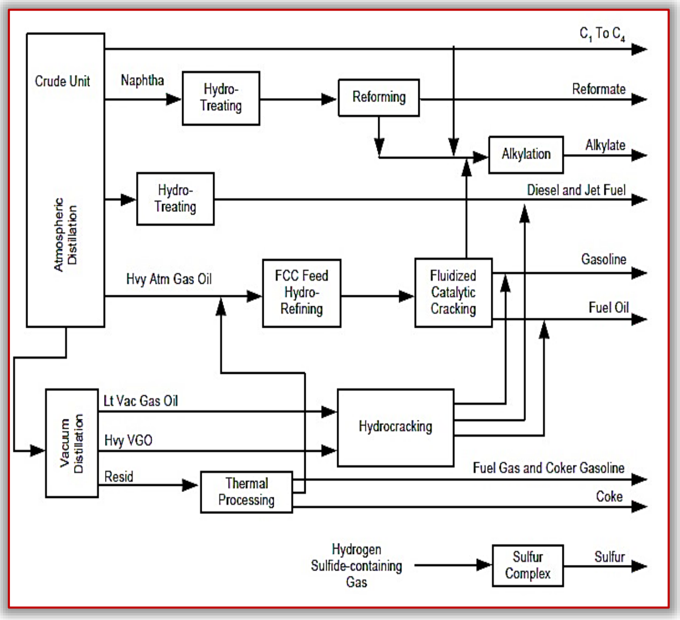

Figure 1. General Layout of a Modern Refinery

Changes in the characteristics of conventional crude oil can be exogenously specified and will trigger changes in refinery configurations and corresponding investments. The future crude slate is expected to consist of larger fractions of both heavier, sourer crudes and extra-light inputs, such as natural gas liquids (NGLs). There will also be a shift towards bitumen, such as the Venezuelan extra heavy crude oil and the bitumen from the Canadian tar sands. These changes will require investment in upgrading, either at field level to process difficult-to-transport heavy crude oil, extra heavy crude oil, tar sand bitumen, either at a field site or at a remote refinery [3, 5, 6, 7].

— Biorefinery

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to the crude oil refinery, which produce multiple fuels and products from crude oil [5, 6]. In fact, there is a renewed interest in the utilization of plant based matter (biomass) as a raw material feedstock for the chemicals industry [8, 9, 10, 11].

Plants offer a unique and diverse feedstock for chemicals. Plant biomass can be gasified to produce synthesis gas; a basic chemical feedstock and also a source of hydrogen for a future hydrogen economy [12]. In addition, the specific components of plants such as carbohydrates, vegetable oils, plant fiber and complex organic molecules known as primary and secondary metabolites can be utilized to produce a range of valuable monomers, chemical intermediates, pharmaceuticals and materials. More generally, biomass feedstocks are recognized by the specific plant content of the feedstock or the manner in which the feedstock is produced [3].

The simplest, cheapest and most common method of obtaining energy from biomass is direct combustion. In fact, the combustion process results in some form of organic residue after their primary use has been fulfilled. These organic residues can be used for energy production through direct combustion or biochemical conversion.

In a manner similar to the crude oil refinery, a biorefinery would integrate a variety of conversion processes to produce multiple product streams such as motor fuels and other chemicals from biomass. In short, a biorefinery would combine the essential technologies to transform biological raw materials into a range of industrially useful intermediates. However, the type of biorefinery would have to be differentiated by the character of the feedstock. For example, the *crop biorefinery* would use raw materials such as cereals or maize and the *lignocellulose biorefinery* would use raw material with high cellulose content, such as straw, wood, and paper waste.

However a word of caution about biomass. The aficionados of biomass use cite the fact that biomass is a carbon-zero feedstock insofar as the carbon dioxide emitted to the atmosphere form the use of biomass is offset by the uptake of carbon dioxide during the growth cycle of the biomass. But there are other, often unmentioned issues that must be addressed.

Biomass also contains varying quantities of metals, including alkali metals, alkaline earth metals, and heavy metals. The alkali metals consist of the chemical elements lithium (li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr). Together with hydrogen they make up Group I of the Periodic Table. On the other hand, the alkaline earth metals are the six chemical elements in Group 2 of the Periodic Table and are beryllium (be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). Finally, the heavy metals are less easy to define but are generally recognized as metals with relatively high density, atomic weight, or atomic number. The common transition metals such as copper (Cu), lead (Pb) and zinc (Zn) are often classed as heavy metals but the criteria used for the definition and whether metalloids (types of chemical elements which have properties in between, or that are a mixture of, those of metals and nonmetals) are included, vary depending on the context. These metals are often found in functional molecules such as the porphyrin molecules which include chlorophyll and which contains magnesium. The presence of these metals requires additional treatment to ensure that release into the environment is mitigated.

By analogy with crude oil, every element of the plant feedstock will be utilized including the low value lignin components. However, the different compositional nature of the biomass feedstock, compared to crude oil, will require the application of a wider variety of processing tools in the biorefinery. Processing of the individual components will utilize conventional thermochemical operations and state-of-the-art bioprocessing techniques. The production of biofuels in the biorefinery complex will service existing high volume markets, providing economy-of-scale benefits and large volumes of by-product streams at minimal cost for upgrading to valuable chemicals.

— **Gasification Refinery**

The most likely option for the integration of alternate feedstock into the refinery is the installation of an on-site gasifier. Thus, such a refinery (often referred to as a gasification refinery) would have, as the center piece, gasification technology as is the case of the Sasol refinery in South Africa [13]. The refinery would produce synthesis gas (from the carbonaceous feedstock) from which liquid fuels would be manufactured using the Fischer-Tropsch synthesis technology [3, 5]. Synthesis gas is used as a source of hydrogen or as an intermediate in producing hydrocarbon derivatives via the Fischer-Tropsch synthesis [12, 14].

In fact, gasification to produce synthesis gas can proceed from any carbonaceous material, including biomass. Inorganic components of the feedstock, such as metals and minerals, are trapped in an inert and environmentally safe form as char, which may have use as a fertilizer. Biomass gasification is therefore one of the most technically and economically convincing energy possibilities for a potentially carbon neutral economy.

Moreover, the gasification of carbonaceous feedstock can provide high purity hydrogen for a variety of uses within the refinery [5, 6]. Hydrogen is used in the refinery to remove sulfur, nitrogen, and other impurities from intermediate to finished product streams and in hydrocracking operations for the conversion of high boiling distillates into low boiling products, such as naphtha, kerosene, and atmospheric gas oil. Hydrocracking and severe hydrotreating require hydrogen which is at least 99% v/v pure, while less severe hydrotreating can use 90% v/v pure hydrogen and above and a current refinery typically requires continuous hydrogen availability [5, 6].

— **Fischer-Tropsch Synthesis**

The synthesis reaction is dependent of a catalyst, mostly an iron or cobalt catalyst where the reaction takes place. There is either a low or high temperature process (LTFT, HTFT), with temperatures ranging between 200 to 240°C for LTFT and 300 to 350°C for HTFT. The high temperature Fischer Tropsch technology uses a fluidized catalyst at 300 to 330°C (625°F). Originally circulating fluidized bed units were used (Synthol reactors). Since 1989 a commercial scale classical fluidized bed unit has been implemented and improved upon.

The reactors are the multi-tubular fixed bed, the slurry or the fluidized bed (with either fixed or circulating bed) reactor. The fixed bed reactor consists of thousands of small tubes with the catalyst as surface-active agent in the tubes. Water surrounds the tubes and regulates the temperature by settling the pressure of evaporation. The slurry reactor is widely used and consists of fluid and solid elements, where the catalyst has no particular position, but flows around as small pieces of catalyst together with the reaction components. The slurry and fixed bed reactor are used in LTFT. The fluidized bed reactors are diverse, but characterized by the fluid behavior of the catalyst. The low temperature Fischer Tropsch technology has originally been used in tubular fixed bed reactors at 200 to 230°C. This produces a more paraffinic and waxy product spectrum than the high temperature technology.

A new type of reactor (the Sasol slurry phase distillate reactor has been developed and is in commercial operation. This reactor uses a slurry phase system rather than a tubular fixed bed configuration and is currently the favoured technology for the commercial production of synfuels.

PRODUCTS FROM ALTERNATE FEEDSTOCKS

Alternate feedstocks such as the biomass-based feedstocks, can be converted into liquid or gaseous forms for the production of electric power, heat, chemicals, or gaseous and liquid fuels though the varying contents of cellulose, hemicellulose, and lignin (Table 3).

Table 1. Amounts (% w/w) of Cellulose, Hemicellulose and Lignin Common Agricultural Residues and Wastes*

Agricultural residue	Cellulose	Hemicellulose	Lignin
Bamboo	41-49	24-28	24-26
Coastal Bermuda grass	25	35.7	6.4
Corn cobs	45	35	15
Corn stover	35	28	16-21
Cotton seed hairs	80-90	5-20	0
Grasses	25-40	35-50	10-30
Hardwood stem	40-50	24-40	18-25
Leaves	15-20	80-85	0
Newspaper	40-55	25-40	18-30
Nut shells	25-30	25-30	30-40
Paper	85-99	0	0-15
Primary wastewater solids	8-15	NA	24-29
Rice straw	40	18	5.5
Softwood stem	45-50	25-35	25-35
Solid cattle manure	1.6-4.7	1.4-3.3	2.7-5.7
Sorted refuse	50-60	10-20	15-20
Sugar cane bagasse	32-48	19-24	23-32
Sweet sorghum	27	25	11
Swine waste	6.0	28	-
Switch grass	30-51	10-50	5-20
Waste papers from chemical pulps	60-70	10-20	5-10
Wheat straw	33-40	20-25	15-20

*Listed alphabetically rather than by any preferences.

Table 2.

Type	Cellulose	Hemicellulose	Lignin	Others*	Ash
Soft wood	41	24	28	2	0.4
Hard wood	39	35	20	3	0.3
Pine bark	34	16	34	14	2
Straw (wheat)	40	28	17	11	7
Rice husks	30	25	12	18	16
Peat	10	32	44	11	6

*Metals content is not differentiated in this analysis.

The predominant conversion processes are direct liquefaction, indirect liquefaction, physical extraction, thermochemical conversion, biochemical conversion, and electrochemical conversion. More generally, the production of biofuels from lignocellulosic feedstocks can be achieved through two different processing routes:

- the thermochemical platform and
- the bioconversion platform (Chapter 14).

While each platform is adequate to the task, depending upon the feedstock, there is no clear candidate for best pathway between the various thermochemical technologies and the biochemical technologies.

Table 3. Summary of the Methods
for the Conversion of Biomass to Fuels.

Biomass		
Extraction		
	Transesterification	Biodiesel
Hydrolysis		
	Fermentation	Biogas
		Ethanol
Gasification		
	Synthesis gas	Biogas
		Hydrogen
		Methanol
		Ethanol
Pyrolysis		Hydrogen
		Bio-oil
Hydrotreating		Diesel

The thermochemical platform typically uses a combination of pyrolysis, gasification, and catalysis to transform the feedstock into gaseous products – one of which is synthesis gas and then into fuels or chemicals. Synthesis gas) (also referred to as syngas) production through pyrolysis is accompanied by the generation of char, which can then be gasified to provide process heat and energy for the thermochemical platform.

On the other hand, the bioconversion platform typically uses a combination of physical or chemical pretreatment and enzymatic hydrolysis to convert lignocellulose into its component monomers. This platform (examples are anaerobic digestion and fermentation) uses biological agents to carry out a structured deconstruction of lignocellulose components and combines process elements of pretreatment with enzymatic hydrolysis to release carbohydrates and lignin from the wood. The advantage of the bioconversion platform is that it provides a range of intermediate products, including glucose, galactose, mannose, xylose, and arabinose, which can be relatively easily processed into value-added bioproducts. The bioconversion platform also generates a quantity of lignin or lignin components; depending upon the pretreatment, lignin components may be found in the hydrolysate after enzymatic hydrolysis, or in the wash from the pretreatment stage.

Once hydrolyzed, six-carbon sugars can be fermented to ethanol using age-old yeasts and processes. Five-carbon sugars, however, are more difficult to ferment; new yeast strains are being developed that can process these sugars, but issues remain with process efficiency and the length of fermentation. Other types of fermentation, including bacterial fermentation under aerobic and anaerobic conditions, can produce a variety of other products from the sugar stream, including lactic acid. Bioconversion proceeds at lower temperatures and lower reaction rates and can offer high selectivity for products. Ethanol production is a biochemical conversion technology used to produce energy from alternate fuel feedstocks, depending upon the type and properties of the feedstock. For ethanol production, biochemical conversion researchers have focused on a process model of dilute acid hydrolysis of hemicelluloses followed by enzymatic hydrolysis of cellulose. Biodiesel production is a biochemical conversion technology used to produce energy from oilseed crops.

Cellulosic materials can be used to produce ethanol which represents an important, renewable liquid fuel for motor vehicles. Production of ethanol from alternate fuel feedstocks is one way to reduce both the consumption of crude oil and environmental pollution. In order to produce ethanol from cellulosic materials, a pretreatment process is used to reduce the sample size, break down the hemicelluloses to sugars, and open up the structure of the cellulose component. The cellulose portion is hydrolyzed by acids or enzymes into glucose sugar that is fermented to ethanol. The sugar derivatives from the hemicellulose feedstocks are also fermented to ethanol.

The fermentation process requires pretreatment of the feedstock by chemical, physical, or biological means to reduce the complex carbohydrates to simple sugars. This type of pretreatment is often referred to as hydrolysis. The resulting sugars can then be fermented by the yeast and bacteria employed in the process. Furthermore, feedstocks that have a high content of starch and sugar are most easily hydrolyzed. Cellulosic feedstocks, including the major fraction of organics in MSW, are more difficult to hydrolyze, requiring more extensive pretreatment. Fermentation is generally used industrially to convert substrates such as glucose to ethanol for use in beverage, fuel, and chemical applications and to other chemicals (e.g., lactic acid used in producing renewable plastics) and products (e.g., enzymes for detergents). Strictly speaking, fermentation is an enzymatically controlled anaerobic process although the term is sometimes more loosely applied to include aerobic processing as well.

The bioconversion platform is an industrial option that might be used in a biorefinery (Chapter 12) for producing fuels from alternate fuel feedstocks using biochemical reactions and/or biochemical agents. For example, fermentation or anaerobic digestion to produce fuels and chemicals from organic sources is a bioconversion platform. The bioconversion platform therefore has the ability to serve as the basis for wood-based biorefining operations, generating value-added bioproducts as well as fuel and energy for the forest sector.

THE RECONFIGURED REFINERY

Over the past three decades, the refining industry has been challenged by changing feedstocks and product slate. In the near future, the refining industry will become increasingly flexible with improved technologies and improved catalysts. The main technological progress will be directed to:

- upgrading viscous feedstocks,
- production of cleaner – less environmentally threatening – transportation fuel production and
- the integration of refining and petrochemical businesses.

Even the tried and true processes [5, 6] will see changes as they evolve [15].

In the integration of refining and petrochemical businesses, new technologies based on the traditional fluid catalytic cracking process will be of increased interests to refiners because of their potential to meet the increasing demand for light olefins. Meanwhile, hydrocracking, due to its flexibility, will take the central position in the integration of refining and petrochemical businesses in 21st century

The typical refinery in the year 2050 will be located at an existing refinery site since economic and environmental considerations may make it difficult and uneconomical to build a new refinery at another site. Many existing refining process may still be in use but they will be more efficient and more technologically advanced and perhaps even rebuilt (reactors having been replaced on a scheduled or as needed basis) rather than retrofitted. However, energy efficiency will still be a primary concern, as refiners seek to combat the inevitable increasing cost of crude oil and refinery operating expenses.

The refinery of the future will have a gasification section devoted to the conversion of carbonaceous feedstocks, such as biomass, to Fischer-Tropsch hydrocarbon derivatives. The biomass refinery of the future will also use multiple feedstocks but also it will be able to shift output from the production of one chemical to another in response to market demands. Given that biomass will be a part of a refinery of the future, refiners may dictate that biomass receives preliminary upgrading at the biomass site before being shipped to the crude oil refinery.

To circumvent these issues, there may be no way out of energy production than to consorting alternative energy sources with crude oil, and not of opposing them. This leads to the concept of alternative energy systems, which is wider-ranging and more meaningful than alternative energy sources, because it relate to the actual transformation process of the global energy system [16]. Alternative energy systems integrate crude oil with other energy sources and pave the way for new systems where refinery flexibility will be a key target, especially when related to the increased use of renewable energy sources.

Low quality vegetable oils and greases are likely to be promising in a short-to-medium term to yield diesel fuel and jet-fuel by means of hydroprocessing triglyceride-based feedstocks. Also, processing pyrolysis oil requires larger efforts in commercial development because of the overall poor quality of the bio-oils, the conventional hydrotreating catalysts are expected to have a considerably lower catalyst life in bio-oil upgrading operations than that observed with a crude oil-based feedstock. While the current generation commercial catalysts are excellent hydroprocessing catalysts, they are optimized for crude oil-based feedstock and, since the bio-oils have significantly different properties than petroleum feedstock, it would be worthwhile to dedicate efforts to developing catalysts specifically designed for upgrading bio-oils.

Most of the biomass conversion processes carried out in a refinery need a high amount of hydrogen in order to remove oxygen and yield high energy density fuels. Although biomass valorization can be performed on current commercially available petroleum-based technology, it should not be forgotten that crude oil and biomass feedstocks are chemically different. Nevertheless, heterogeneous catalysis, which has made it possible to convert efficiently crude oil-derived resources to fuels, will also be able to provide the necessary technology to get similar fuels starting from biomass feedstocks providing a new catalyst technology is developed [17].

Note:

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