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SPECIAL FEATURES

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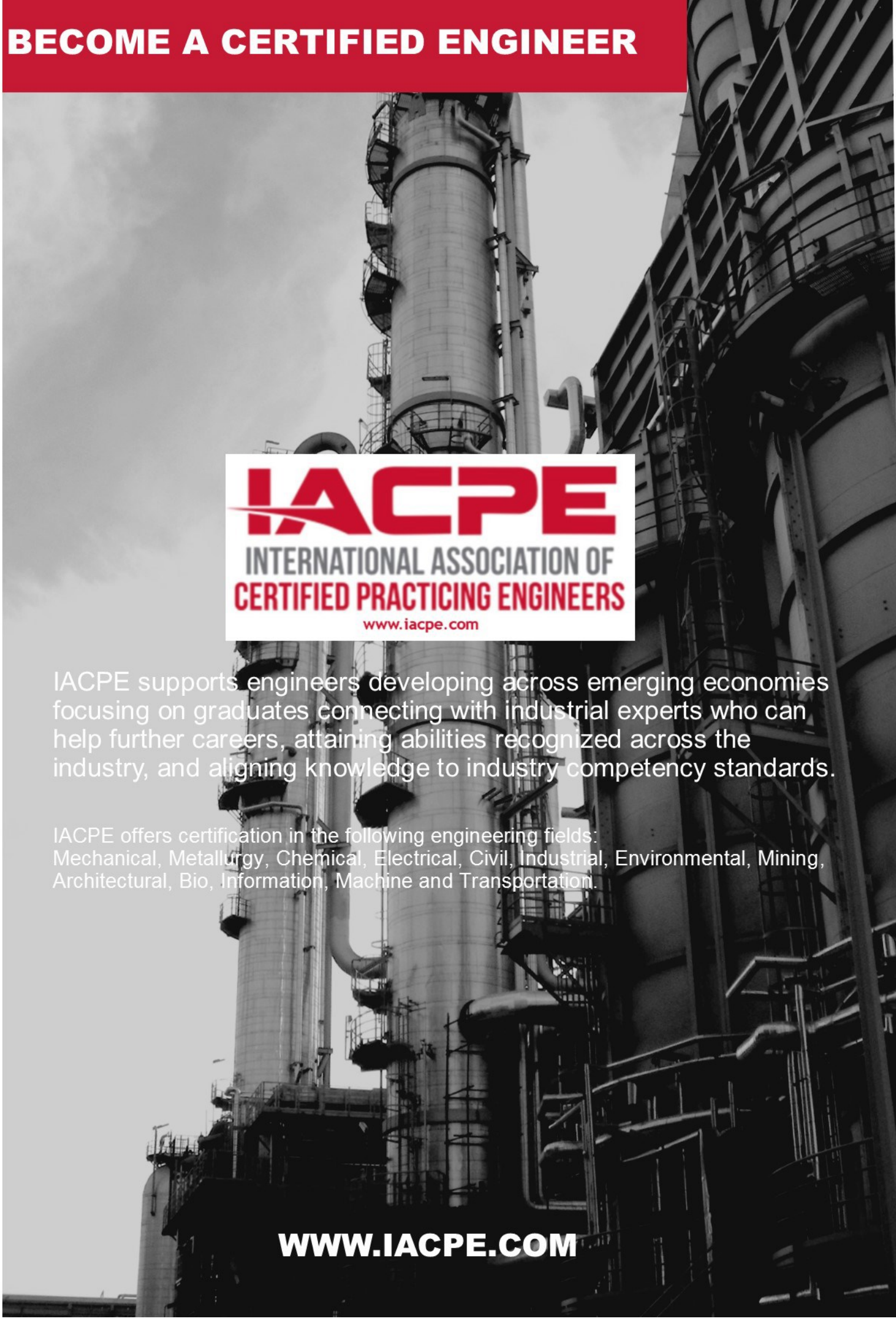

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Green Hydrogen Gas (GH2) Renewable Future Clean Fuel

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Nowadays, climate crisis is an important environmental impact in worldwide. This worst environmental case comes from greenhouses gases (GHG) emissions mainly such as: CO2 gas, NOX gas from stack of industry furnaces, combustion exhaust pipes of transportation vehicles & ships & trains & airplanes caused by using non-renewable fossil products (Petroleum products, coal), waste water evaporation ponds, etc. in which make global warming to produce climate crisis of environmental impacts for examples: Unseasonal heavy floods and storms , Lack of normal raining and long dry years in different countries. Important scenarios to encounter climate crisis include to replace non-renewable energy by renewable energy in which is known as energy transition or mitigate it by changing these GHG to other valuable products in which prevent to produce more GHG. These action plans are known as: decarbonization techniques or net zero carbon emission in which is fully compatible with Paris agreement of United Nations Climate Change Conference (UNCCC) and was signed in 2016 by 196 parties (including European Union) .Parties should even reach net zero by the middle of the 21st. century. To stay below 1.5 °C of global warming, GHG emissions needed to be cut by roughly 50% by 2030. [1] After Paris agreement many developed and developing countries have defined their different roadmaps to reach energy transition to reach .One of more important of these action plan is producing hydrogen from other non-fossil based sources such as water , biosyngas , as an accelerating revolution footprint of clean energy future production in which is known as Renewable Future Clean Fuel of the worldwide, and has many benefits for environment such as its type of combustion products(only steam) from stacks or exhaust pipe instead of CO2, NOX, and SOX as air pollution gases of fossil based products. Also we could get electricity from it to use in FCEV (fuel cell electrical vehicle). In this monograph subjects related to GH2 (main process & technologies), in addition describes a little different types of hydrogen based on its process, feedstock, and technologies too [2].

Keywords: green hydrogen gas (GH2), greenhouses gases (GHG) emission, climate crisis, non-renewable and renewable energy, net zero carbon emission and decarbonization, energy transition

Introduction (why green hydrogen gas, GH2?)

Regardless of dealing with the consequences of climate change due to the use of fossil fuels, hydrogen gas with the non-based fossil feedstock source, it may play a crucial factor to help countries achieve their net zero (carbon) emission (NZE) long terms decarbonization targets in energy transition and in line with the Paris agreement. One of acceptable alternative to prevent GHG emission is producing and using renewable gas energy such as green hydrogen gas (GH2) production instead of non-renewable hydrocarbon energy products such as: fuel oil, diesel, LPG, natural gas, gasoline as the main currently energy sources (including more environmental pollutants). The production and using of GH2 gas have many environmentally benefits. Firstly, to produce GH2 we need water and renewable electricity for example solar, wind or hydropower .Its process is known as electrolysis .Secondly, the combustion product of green hydrogen gas is only steam (instead of carbon dioxide as the worst type of GHG and other pollutants of burning fossil products). Anyway, the other type of producing energy of green hydrogen gas is electricity generation by oxidation of it to produce electron (electricity) in which is used in FCVE. Then, these may be summarized as below items [3]:

- Prevention of GHG emission to mitigate global climate crisis

Table 1 - Physical properties of hydrogen gas (H2) [4]

Row	Properties	Value	Unit
1	Physical state in gas (and liquid)		
2	Flammable rage in air	4-75	Vol.%
3	Molecular weight	2.02	Gr.
4	Specific gravity(air=1)	0.0696	Gr/cm3
5	Specific heat at constant pressure , Cp	14.29	j/g-k
6	Specific heat at constant pressure , Cv	10.16	j/g-k
7	Density of liquid hydrogen	0.071	Kg/L
8	Volumetric lower heating value (LHV)	8.52	Mj/L
9	Temperature for transportation and storage	-253	C

Table 2 - Comparison properties of hydrogen gas (H2) with the other Fossil products [4]

Row	Fuel	Energy Density (MJ/KG)	Flame Speed cm/sec
1	Hydrogen	119.7	300-400
2	Natural Gas	45.8	30-40
3	Gasoline	44.8	
4	Diesel	42.5	

- Best alternative replacement of non-renewable energy feedstock with renewable energy feedstock for future
- A practical action plan in decarbonization and net zero carbon emission in energy transition of the worldwide and in line with the Paris agreement

Basic hydrogen gas (H2) properties
Some of physical properties of hydrogen gas and comparison with other non-renewable products are following as in table-1, table-2, [4].

Hydrogen gas (H2) conversion data
There is hydrogen gas conversion data in the below table-3 [4].

SCF (standard cubic foot) and SM3 (standard cubic meter) gas measured at 1 atmosphere and 21 degree centigrade.

Nm3 (normal cubic meter) gas measured at 1 atmosphere and 0 degree centigrade.

Hydrogen gas COLOUR CLASSIFICATION
There are a usual color classifications of hydrogen gas production too in which are summarized in the table-4 as follows in many different references [5].

Hydrogen GAS (H2) common processes
There are many types of process to produce hydrogen gas such as: steam methane reforming (SMR), coal/petroleum coke/biomass gasification, electrolysis of water (green hydrogen gas, GH2) … regarding to a few below reactions in the table-5, [5].

Table 3 - Hydrogen gas (H2) conversion data [4]

Hydrogen	Weight		Gas		Liquid	
	Pounds	Kilograms	Cubic Feet	Cubic Meters	Gallons	Liters
	Lb	Kg	SCF	Nm3	Gal	L
1 Pound	1	0.4536	192	5.047	1.6928	6.408
1 Kilogram	2.205	1	423.3	11.126	3.733	14.128
1 SCF Gas	0.005209	0.002363	1	0.02628	0.00882	0.03339
1 Nm3 Gas	0.19815	0.08988	38.04	1	0.3355	1.2699
1 Gal Liquid	0.5906	0.2679	113.41	2.981	1	3.785
1 L Liquid	0.15604	0.07078	29.99	0.7881	0.2642	1

Table 5 - Different process types of hydrogen gas (H2) [5]

Process	Type	Reaction	Desciption
Steam Methane Reforming (SMS)	✖	$CH_4 + H_2O \rightarrow CO + 3\ H_2$ / $CO + H_2O \rightarrow CO_2 + H_2$	H_2 Is Produced Form Natural Gas [Mostly Methane (CH_4)] & Currently The Cheapest Source Of Industrial H_2. Nearly 50% Of The World's H_2 Is Being Produced By This Method.
Methane Pyrolysis	✔	$CH_4 \rightarrow C + 2\ H_2$	Here Also H_2 Is Produced From Natural Gas [Mostly Methane (CH_4)]. H_2 Separation Occurs In One Step Via Flow Through A Molten Metal Catalyst In A "Bubble Column". It Produces Low-Cost H_2 But Requires High Temperatures (1065 °C). It Also Produces The Industrial Quality Solid Carbon Which Is A Green Waste.
Partial Oxidation	✖	$C_xH_y + x/2\ O_2 \rightarrow x\ CO + y/2\ H_2$ [$C_{12}H_{24} + 6\ O_2 \rightarrow 12\ CO + 12\ H_2$ $C_{24}H_{12} + 12\ O_2 \rightarrow 24\ CO + 6\ H_2$]	In This Process H_2 Production Is Done From Heavy Hydrocarbons, Which Are Unsuitable For Above Two Processes. It First Generates H_2 And CO Rich Syngas & Then More H_2 And CO_2 Are Obtained Via The Water-Gas Shift Reaction.
Plasma Reforming	✔	$C_xH_y \rightarrow xC + y/2\ H_2$	Also Knwon As "The Kværner Process (1980)" & Produces H_2 As Well As Carbon Black From The Liquid Hydrocarbons (C_xH_y). CO_2 Is Not Produced In The Process.
Coal/ Petroleum Coke	✖	$3\ C\ (Coal) + O_2 + H_2O \rightarrow H_2 + 3\ CO$ $CO + H_2O \rightarrow CO_2 + H_2$	The Process Of Coal Gasification Uses Coal, Steam And Oxygen To Form A Gaseous Mixture Of H_2 And Carbon Monoxide Which Again Is Made To React & Produce More H_2 Along With CO_2.
Electrolysis	✔ ✖	$2\ H_2O \rightarrow 2\ H_2 + O_2$	H_2 Is Produced By Splitting The Water Molecule (H_2O) Into Its Components H_2 And O_2 Using Electricity. When The Source Of Electricity Is Green, The H_2 Produced Is Referred As Green H_2. However, This Method Is Generally Expensive Than Fossil Fuel Based Production Methods.
Depleted Oil Wells	✖	N/A	Injecting Appropriate Microbes Into Depleted Oil Wells Allows Them To Extract H_2 From The Remaining, Unrecoverable Oil In The Wells.

Of course, many other commercial developers have defined a variety of hydrogen advanced process technologies such as : Thermolysis (Haffner Energy), Photolysis (SunHydrogen) , Photocatalytic water splitting (SPARC Hydrogen) , Plasmalysis (lenesys) , Dark Fermentation of organic matter (CEMVITA) etc .

What is green hydrogen gas (GH2)?

Green hydrogen gas (GH2) is a type of hydrogen production process that shall be produced by electrolysis of water by renewable direct current (DC) electricity in which comes from renewable power electricity sources such as: solar, wind, hydropower. Simply in the electrolysis process, two electrodes inside of water should be connected to a DC source of electricity. In the reaction the water is dissociated to hydrogen gas (H2) and oxygen gas (O2). From the electrode in which the hydrogen gas (H2) is released and collected, it is known as cathode and this hydrogen gas. And from the other electrode in which the oxygen gas (O2) is released and collected, it is known as anode.

H2O + electricity (solar, wind …) = GH2 + O2

Equation 1 .Electrolysis of water by renewable electricity to produce GH2

Because of using only water and renewable electricity (solar, wind…) in this process hydrogen production instead of using non-renewable fossil feedstock, it is known as, green hydrogen gas (GH2) [6].

What technologies are used in driving Green hydrogen gas (GH2)?

Green hydrogen gas quickly evolved as clean future energy regarding to climate crisis. There are few steps needed to produce, store and finally use green hydrogen gas in supply chain of green hydrogen gas as follows:

1st step. **Electrolysis**: It is the first step to produce green hydrogen gas by a dissociation chemical reaction. It involves dissociation of water into hydrogen gas and oxygen gas by using electricity generation from renewable sources such as wind, solar, hydropower in which is known as: electrolysis, figure-1. The most famous commercialised types of electrolyser technologies using in electrolysis dissociation reaction are Proton Exchange Membrane (PEM) electrolyser, alkaline electrolyser, and Solid Oxide Electrolysers (SOE) [7].

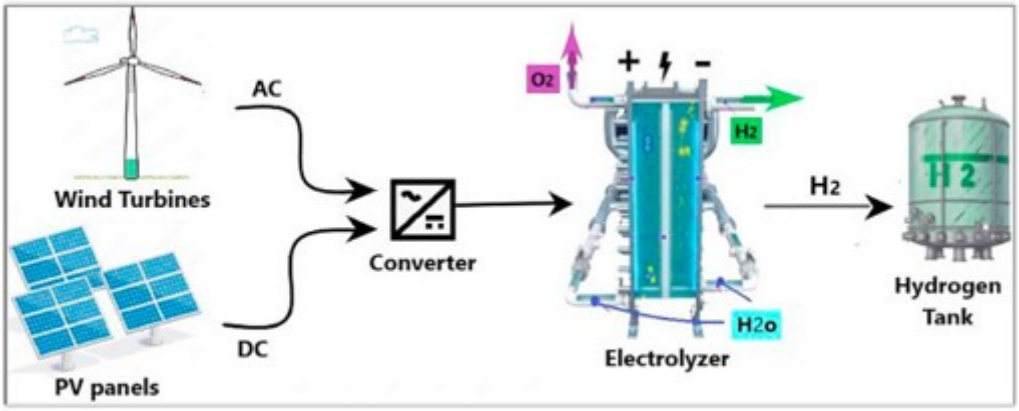


Figure 1.Schematic of GH2 production from renewable energy sector [8]

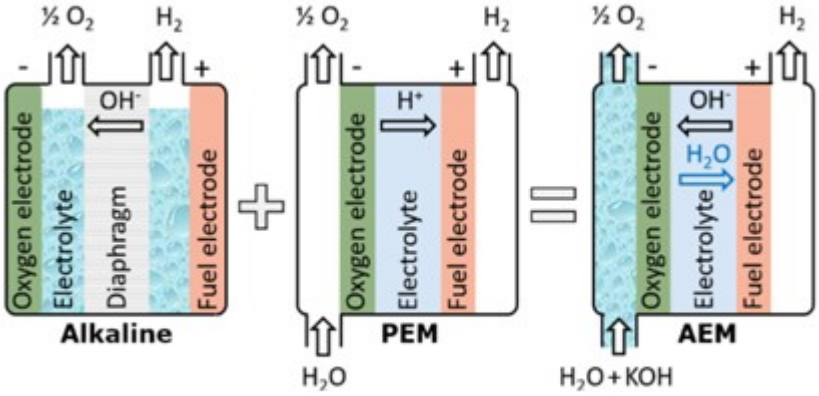


Figure 2-Schematic Alkaline, PEM, AEM water electrolysis technologies [9]

1.1 **Alkaline Electrolyser Technology**: It is the most established and widely used type in industrial scale. It uses a liquid alkaline solution (as usual potassium hydroxide) as the electrolyte. Alkaline electrolyser is known for its durability and cost-effectiveness [8].Alkaline water electrolysis is considered the standard for large –scale H2 production due to its technological maturity and lower investment costs compared to PEM technology. This technology may not be the best option for balancing variable renewable energy sources like wind and solar PV.

1.2 **Proton Exchange Membrane (PEM) Electrolyser Technology**: PEM electrolyser uses a solid polymer electrolyte and pure water. It is known for its high efficiency and ability to operate at higher current densities and pressures and in industrial scale. PEM electrolyser seems to be the best solution for combining solar & wind energy with green hydrogen production [8].PEM electrolyser are more efficient than alkaline technology and produces higher green hydrogen gas (GH2) ,figure-2 [9] .

1.3 **Solid Oxide Electrolysis Cell (SOEC) Technology**: This type of electrolyser operates at high temperatures (typically around 700-800°C) and uses a solid ceramic electrolyte. SOEC is highly efficient and can directly use heat from industrial processes or concentrated solar power. So, this type of electrolyser is now in the early stage of development and is more complex and more expensive than alkaline and PEM electrolyser types but it is in industrial scale [10].Its efficiency is 80-90% in which surpasses other electrolysis but its high operating temperature is remarkable to start-up time and lower durability and short lifetime of electrolyser due to high operating temperature are main challenges despite the higher of its efficiency ,figure-3 [11] .

1.4 **Anion Exchange Membrane (AEM) electrolysis Technology**: The chemistry of AEM electrolysers is the same as for alkaline electrolysers. Although AEM electrolysers are in industrial scale but can potentially offer “the best of both worlds” when compared to alkaline electrolysers and PEM electrolysers, significant technology development is still required for the technology to become competitive but needs a lower concentration alkaline solution than alkaline electrolyser and less energy consumption and more efficient and more purity of generated H2.The performance of AEM electrolyser in water splitting is lower than PEM technology type.

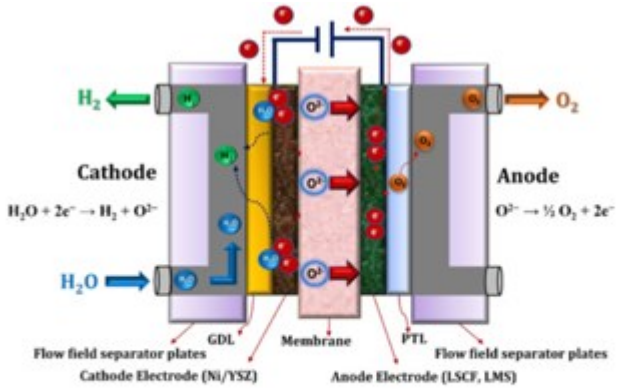


Figure 3-Schematic SOEC water electrolysis technology [11]

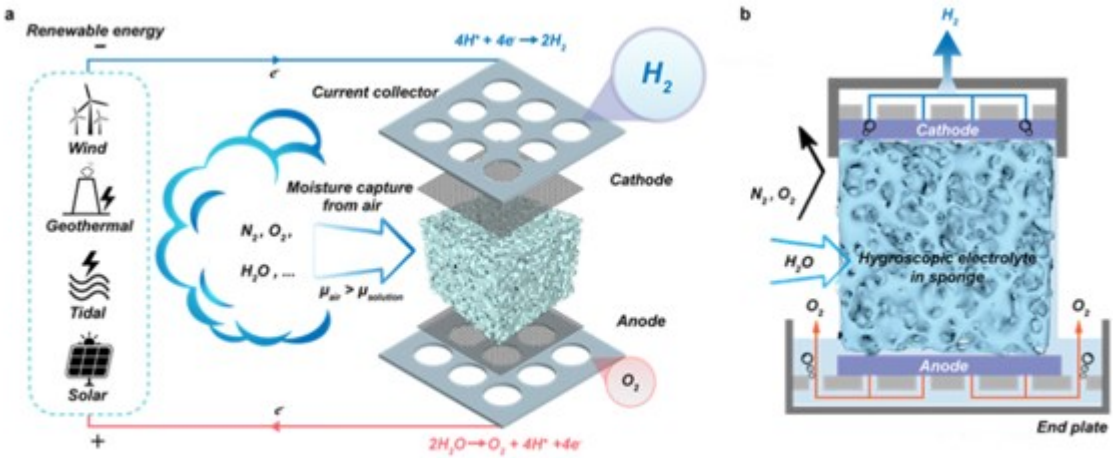


Figure 4-Schematic water (moisture) electrolysis of DAE technology [12]

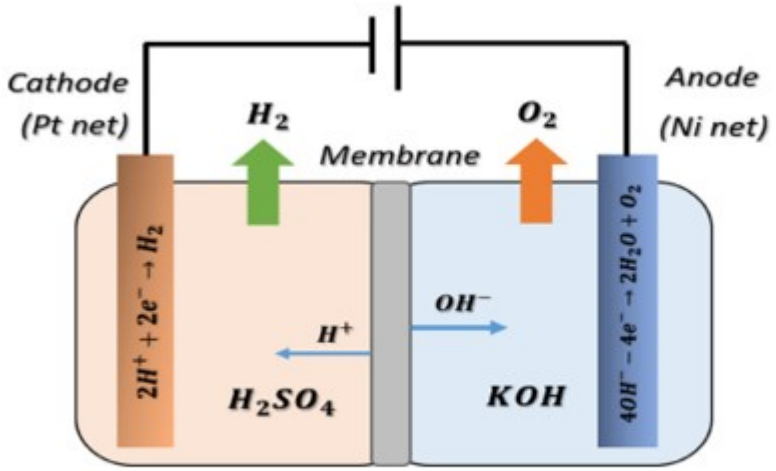


Figure 5-Schematic Acidic/Alkaline amphoteric water electrolysis technology [13]

1.5 ** Direct Air Electrolysis (DAE) Technology**: This technology produces GH2 from moisture in air by solar or wind electricity) .This new type of technology may produce GH2 under dry conditions (relative humidity of 4%), figure-4 [12].

1.6 **Acidic/Alkaline Amphoteric Electrolyser Technology**: This type of technology uses less energy consumption and a higher rate of H2 generation compared to alkaline and AEM technologies and less expensive than PEM technology and have greater efficiency than MCEC technology ,figure-5 [13] .

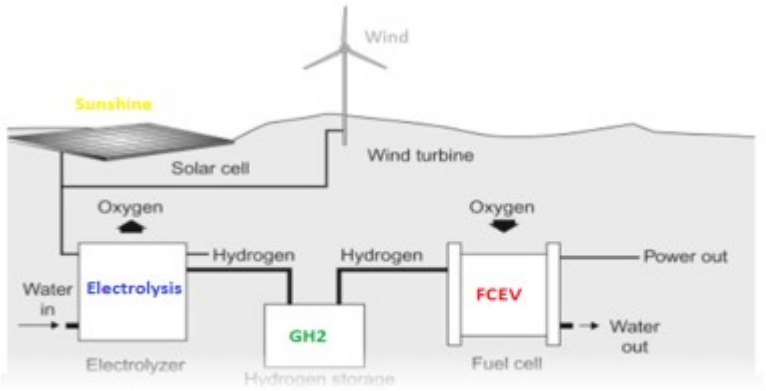


Figure 6. Fuel Cell as a power system energy storage technology [15]

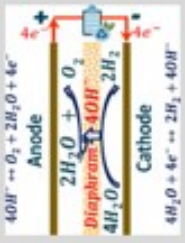
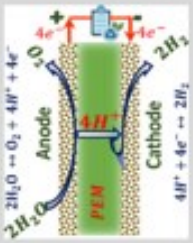
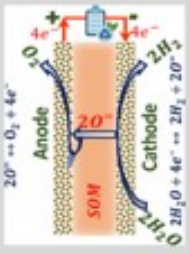
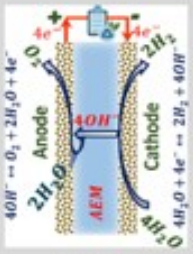
2nd. Step **Fuel Cells**: Hydrogen fuel cells is a more reliable using to convert hydrogen gas into electricity, with water and heat as the only its by-products,figure-6. This ability is used in various applications (backup power systems, portable power sources), especially vehicles (Fuel cell electric vehicles, FCEVs) [14] [15].

3rd. step** Hydrogen Storage and Transportation**: The long-term storage and transportation of hydrogen is another very important point in its supply chain. Methods in this step are compressing hydrogen, liquefaction of hydrogen, changing to other chemical carriers like ammonia, injection to natural gas pipeline [16].

4th step. **Integration with Renewable Energy**:
It is also possible to manage the production and consumption of this renewable energy sources by producing green hydrogen from excess renewable electricity and use it in the form of hydrogen gas in days when it is not possible to supply it due to weather conditions (low sunlight/low wind speed/low production of hydroelectric power plants) [17].

Table 6-Properties of conventional water electrolysis technologies to produce GH2

Rough characteristics of the conventional water electrolysis techniques

Technology readiness level (TRL)	Mature/commercialised ⟵ ⟶ R & D			
Electrolysis technology	Alkaline electrolysis (AE)	Proton exchange membrane (PEM) electrolysis	Solid oxide membrane (SOM) electrolysis	Anion exchange membrane (AEM) electrolysis
Schematic diagram and operating principle				
Operating temperature, °C	70–90	50–80	600–1000	40–60
Operating pressure, bar	~Atmospheric	<40	<5	<35
Nominal voltage, V	1.8–2.4	1.8–2.2	0.80–1.6	1.4–2.0
Nominal current density, A/cm^2	0.2–0.5	0.6–3.0	0.1–3.9	0.2–2.0
Type of Electrolyte/ membrane	KOH solution (25–30 wt.%)	Generic PEMs (PFSA)	Yttria-Stabilised zirconia (YSZ) or gadolinium-doped ceria (GDC)	Generic AEMs (DVB polymers)
Commercial separator	Zirfon™, polysulfone, and polyphenylene sulphide polymers	Nafion™	YSZ/GDC Pellets	Fumatech™
Common types of cathode/ anode electrocatalysts	Nickel-coated perforated stainless steel	Iridium/platinum	Nickel-YSZ/LSM (lanthanum strontium manganite)-YSZ	Nickel foam or carbon cloth
Cell nominal efficiency (HHV), %	50–80	50–83	80–100	52–67
Specific energy consumption, kWh/Nm^3	5.0–5.9	5.0–6.5	3.7–3.9	Unknown
Hydrogen purity, %	99.5–99.9998	99.9–99.9999	99.9	99.9–99.9999
Stack lifetime, h	<90,000	<20,000	<20,000	<5000
Stack cost, USD/kW)	270	400	>2000	Unknown

Conclusion

Green hydrogen gas (GH2) by using water and renewable electricity (solar, wind, hydropower) with relevant different technologies table-6, [18] has a high potential to decarbonize several sectors, including heavy industries, transportations, and buildings,… and making it a key player in the transition to a sustainable decarbonization energy and net zero carbon emission to mitigate climate crisis and replacing by non-renewable fossil in future to prevent global warming [19] .

Abbreviations

GHG: Green House Gas
GH2: Green Hydrogen Gas
FCEV: Fuel Cell Electrical Vehicle
UNCCC: United Nations Climate Change Conference
NZE: Net Zero (Carbon) Emission
NUL: Nova University Lisbon
SCF: Standard Cubic Foot
SM3: Standard Cubic Meter
CO2: Carbon Dioxide
NOX: Nitrogen Dioxide
SOX: Sulphur Dioxide
LPG: Liquid Petroleum Gas
PEM: Proton Exchange Membrane Electrolyser
SOEC: Solid Oxide Electrolysis Cell
AEM: Anion Exchange Membrane

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Professor Ana Luisa Fernando activates in FCT-NOVA University in Lisbon Portugal. She is an expert and has overseen bio-energy teaching master courses in master & PhD degrees and projects direction especially in changing biomass to energy many years in NOVA University Lisbon (NUL) and main speaker in European and international events of sustainable energy technologies in energy transition.

Review of Bio Diesel Technology

Karl Kolmetz

Introduction

Biodiesel refers to the fuel commonly called an ester, or fatty acid methyl esters (FAME) produced from renewable fats, oils, and/or greases that meets the most current ASTM International Standard D6751. Biodiesel is most used as a blend with petroleum diesel fuels, including ASTM International Standard D975 grades No. 1 and No. 2 diesel fuel or ASTM International Standard D396 heating oil, as well as other distillate and residual fuel oils.

The number following the letter "B" in a biodiesel blend indicates the percent by volume (vol %) of biodiesel in 1 gallon of fuel (e.g., B20 is 20% biodiesel by volume); the remainder of the fuel can be No. 1 or No. 2 diesel, heating oil, or any other distillate or residual fuel. Pure (or neat) biodiesel is called B100.

Biodiesel is produced from plant oils, animal fats, recycled cooking oils, and/or greases and has several advantages:

- Renewable, with a much lower carbon intensity/life cycle greenhouse gas emissions profile than petroleum diesel fuel, such that it reduces global warming emissions.
- Can be used at up to at least 20% blend level in most diesel equipment with zero or minor modifications.
- Compatible with all new on- and off-road diesel engines—often called "new technology diesel engines" (NTDEs)—and burners and backward-compatible with most equipment.
- Demonstrated to reduce tailpipe soot emissions and other criteria pollutants from older (e.g., legacy) engines without modern emission controls, as well as from industrial boiler and home heating systems.
- Nontoxic, biodegradable, and suitable for sensitive environments. Degrades more rapidly than diesel fuel, minimizing the environmental consequences of biofuel spills.
- Renewable fuel, obtained from vegetable oils or animal fats.
- Lower emissions of contaminants: carbon monoxide, particulate matter, polycyclic aromatic hydrocarbons, aldehydes.
- Lower health risk, due to reduced emissions of carcinogenic substances.
- No sulfur dioxide (SO2) emissions.
- Higher flash point (100C minimum).

There are certain disadvantages of using biodiesel as a replacement for diesel fuel
that must be taken into consideration:

- Slightly higher fuel consumption due to the lower calorific value of biodiesel.
- Slightly higher nitrous oxide (NOx) emissions than diesel fuel.
- Higher freezing point than diesel fuel. This may be inconvenient in cold climates.
- It is less stable than diesel fuel, and therefore long-term storage (more than six months) of biodiesel is not recommended.
- May degrade plastic and natural rubber gaskets and hoses when used in pure form, in which case replacement with Teflon components is recommended.
- It dissolves the deposits of sediments and other contaminants from diesel fuel in storage tanks and fuel lines, which then are flushed away by the biofuel into the engine, where they can cause problems in the valves and injection systems. In consequence, the cleaning of tanks prior to filling with biodiesel is recommended.

It must be noted that these disadvantages are significantly reduced when biodiesel is used in blends with diesel fuel.

The raw materials for biodiesel production are vegetable oils, animal fats and short chain alcohols. The oils most used for worldwide biodiesel production are rapeseed (mainly in the European Union countries), soybean (Argentina and the United States of America), palm (Asian and Central American countries) and sunflower, although other oils are also used, including peanut, linseed, safflower, used vegetable oils, and animal fats. Methanol is the most frequently used alcohol although ethanol can also be used.

Since cost is the main concern in biodiesel production and trading (mainly due to oil prices), the use of non-edible vegetable oils has been studied for several years with good results.

Besides its lower cost, another undeniable advantage of non-edible oils for biodiesel production lies in the fact that no foodstuffs are spent to produce fuel. These and other reasons have led to medium- and large-scale biodiesel production trials in several countries, using non-edible oils such as castor oil, tung, cotton, jojoba and jatropha. Animal fats are also an interesting option, especially in countries with plenty of livestock resources, although it is necessary to carry out preliminary treatment since they are solid; furthermore, highly acidic grease from cattle, pork, poultry, and fish can be used.

Microalgae appear to be a very important alternative for future biodiesel production due to their very high oil yield; however, it must be considered that only some species are useful for biofuel production.

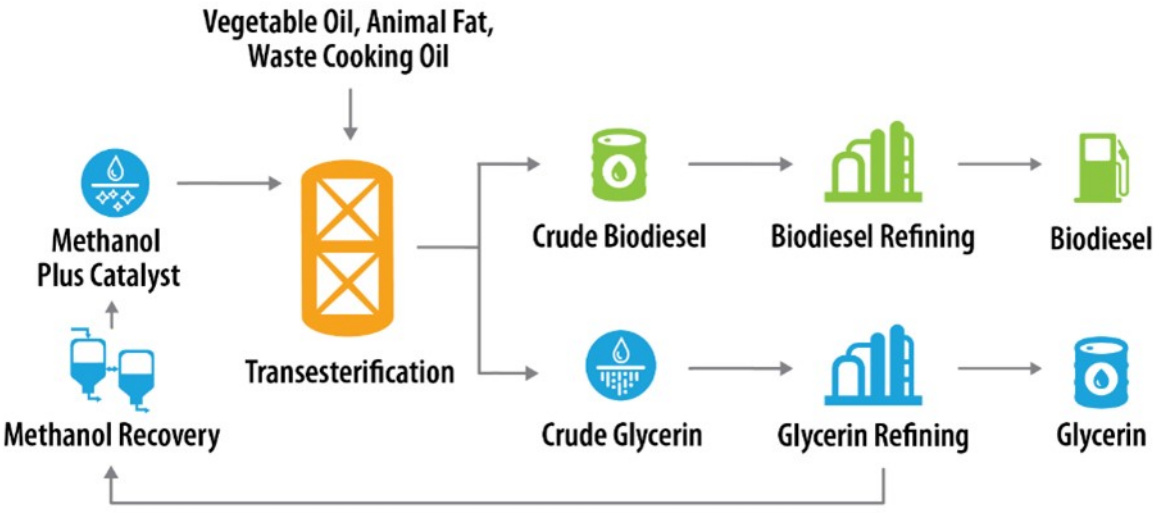
Although the properties of oils and fats used as raw materials may differ, the properties of biodiesel must be the same, complying with the requirements set by international standards.

Biodiesel is a commercially available, lower-carbon-intensity fuel for use in diesel engines, boilers, and home heating oil systems. It can directly replace or be blended with distillate and residual fuel oils, like diesel fuel or heating oil. Biodiesel is manufactured from plant oils (e.g., soybean oil, cottonseed oil, canola oil, corn oil, palm oil), recycled/used cooking greases (e.g., yellow grease), animal fats (e.g., beef tallow, pork lard, poultry fat), or various combinations of these feedstocks. In addition, other oilseed crops are being commercialized.

Biodiesel Process

The biodiesel production process is known as transesterification, which converts these oils, fats, and/or greases into long-chain monoalkyl esters, or biodiesel. The esters are commonly referred to as fatty acid methyl esters (FAME) when methanol is used in the transesterification reaction. Virtually all biodiesel production today uses methanol. Roughly speaking, 100 pounds of oil, fat, and/or grease is reacted with 10 pounds of alcohol, usually methanol (although production from other alcohols is possible), in the presence of a catalyst (usually sodium methoxide) to form 100 pounds of biodiesel and 10 pounds of glycerine (or glycerol). Crude glycerine is a coproduct of the biodiesel process and has economic value. Biodiesel is a legally registered fuel and fuel additive with the U.S. Environmental Protection Agency (EPA).

Biodiesel is a fuel made from vegetable oil through a chemical reaction called



transesterification. During transesterification, the -O-R group of an ester (R'COOR) and the -O-R" group of an alcohol (R"-OH) trade places, changing one *ester* (R'COOR) into another (RCOOR").

Vegetable oil is a triglyceride (also called triacylglycerol), a glycerin (or glycerol) molecule connected via ester bonds to three fatty acid molecules (RCOOH). During the reaction, the fatty acids of the triglyceride molecule are cleaved and attached to the alkyl group (the part made of carbon and hydrogen) of the alcohol to form fatty acid alkyl esters (in our case, fatty acid methyl esters or FAMEs), which are biodiesel.

To speed up the reaction, a base catalyst, typically sodium hydroxide (NaOH) or potassium hydroxide (KOH), is used. Animal fats are also triglycerides and therefore can also be made into biodiesel.

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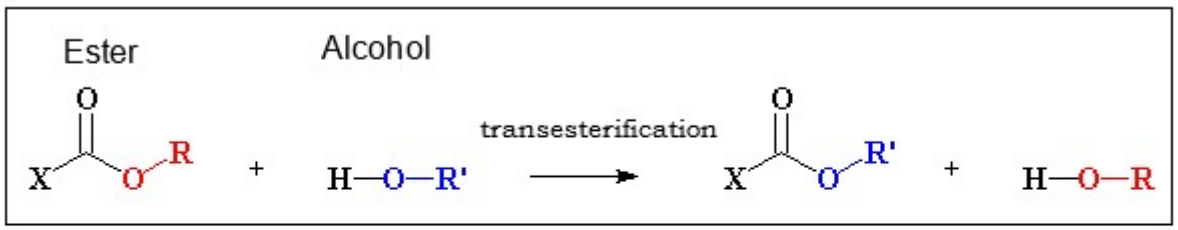
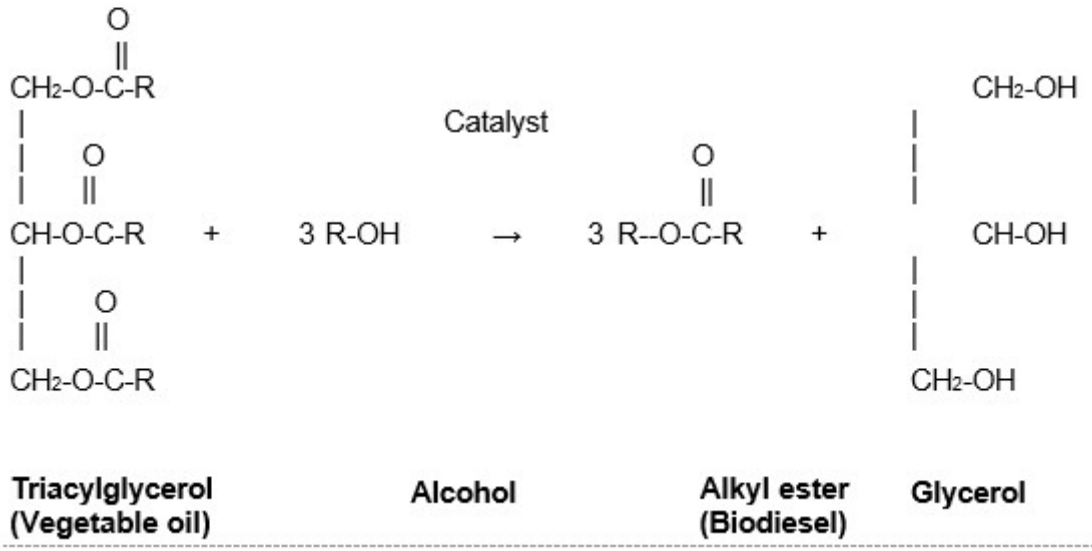
For the transesterification to occur, usually 6 moles of alcohol are used for every mole of triglyceride, which is more than the equation indicates. The reason is that the reaction is desired to proceed in the direction of the arrow, i.e., to the right. In other terms, the equilibrium of the reaction needs to be shifted toward the right side of the equation.

As the term "equilibrium" indicates, not all reactions easily proceed to completion and after some time the starting materials and reaction products are present in constant amounts (the equilibrium has been attained). In many cases, the fact that a reaction can proceed in the reverse fashion (from right to left in the equation) also plays a role in the formation of the equilibrium.

To force the equilibrium in the direction of the products (as is almost always desired), one or more parameter(s) of the reaction may need to be changed. Such parameters include the molar ratio as well as others such as temperature, pressure and use of a catalyst.





Typical proportions for the chemicals used to make biodiesel are:

Reactants	•Fat or oil (e.g. 100 kg soybean oil)
	•Primary alcohol (e.g. 10 kg methanol)
Catalyst	•Mineral base (e.g. 0.3 kg sodium hydroxide)
Neutralizer	•Mineral acid (e.g. 0.25 kg sulfuric acid)

The options for the triglyceride choice are many. Among the vegetable oils sources are soybean, canola, palm, and rape. Animal fats are products of rendering operations. They include beef tallow, lard, poultry fat, and fish oils. Yellow greases can be mixtures of vegetable and animal sources. There are other less desirable, but also less expensive triglyceride sources such as brown grease and soap stock.

The free fatty acid content affects the type of biodiesel process used, and the yield of fuel from that process. The other contaminants present can affect the extent of feedstock preparation necessary to use a given reaction chemistry.

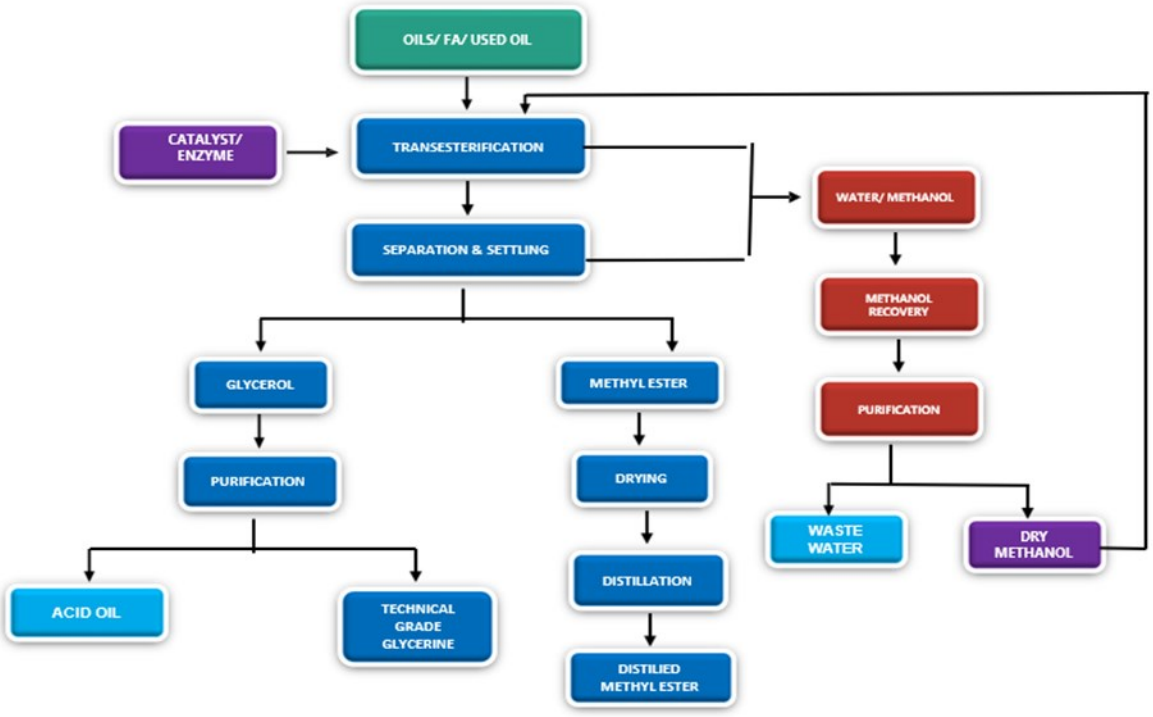
Alcohol: The most used primary alcohol used in biodiesel production is methanol, although other alcohols, such as ethanol, isopropanol, and butyl, can be used. A key quality factor for primary alcohol is the water content. Water interferes with transesterification reactions and can result in poor yields and high levels of soap, free fatty acids, and triglycerides in the final fuel. Unfortunately, all lower alcohols are hygroscopic and are capable of absorbing water from the air.

Neutralizers are used to remove the base or acid catalyst from the product biodiesel and glycerol. If you are using a base catalyst, the neutralizer is typically an acid, and vice versa. If the biodiesel is being washed, the neutralizer can be added to the wash water. While hydrochloric acid is a common choice to neutralize base catalysts, as mentioned earlier, if phosphoric acid is used, the resulting salt has value as a chemical fertilizer.

Batch Processing

The simplest method for producing alcohol esters is to use a batch, stirred tank reactor. Alcohol to triglyceride ratios from 4:1 to 20:1 (mole:mole) have been reported, with a 6:1 ratio most common. The reactor may be sealed or equipped with a reflux condenser. The operating temperature is usually about 65°C, although temperatures from 25°C to 85° C have been reported.

The most used catalyst is sodium hydroxide, with potassium hydroxide also used. Typical catalyst loadings range from 0.3 % to about 1.5%. Thorough mixing is necessary at the beginning of the reaction to bring the oil,

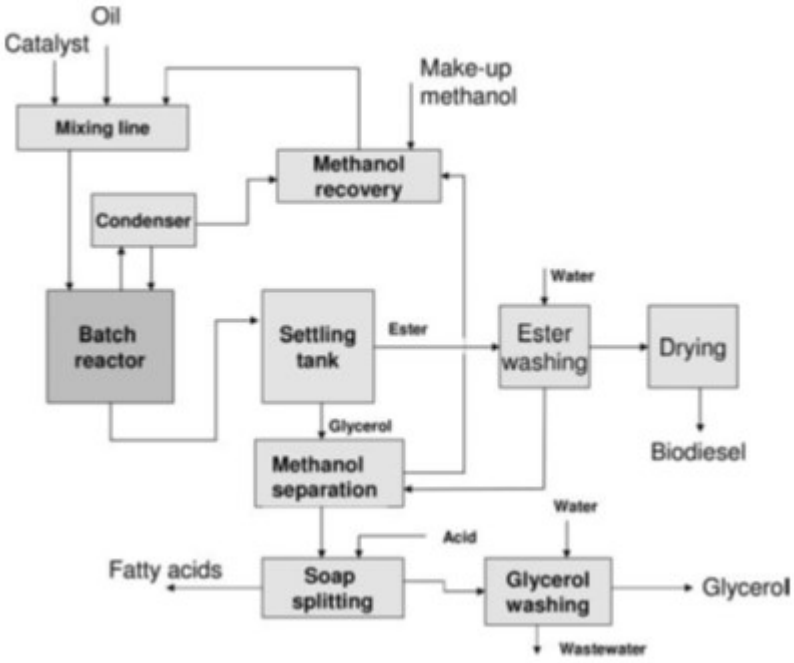


catalyst and alcohol into intimate contact. Towards the end of the reaction, less mixing can help increase the
extent of reaction by allowing the inhibitory product, glycerol, to phase separate from the ester – oil phase. Completions of 85% to 94 % are reported.

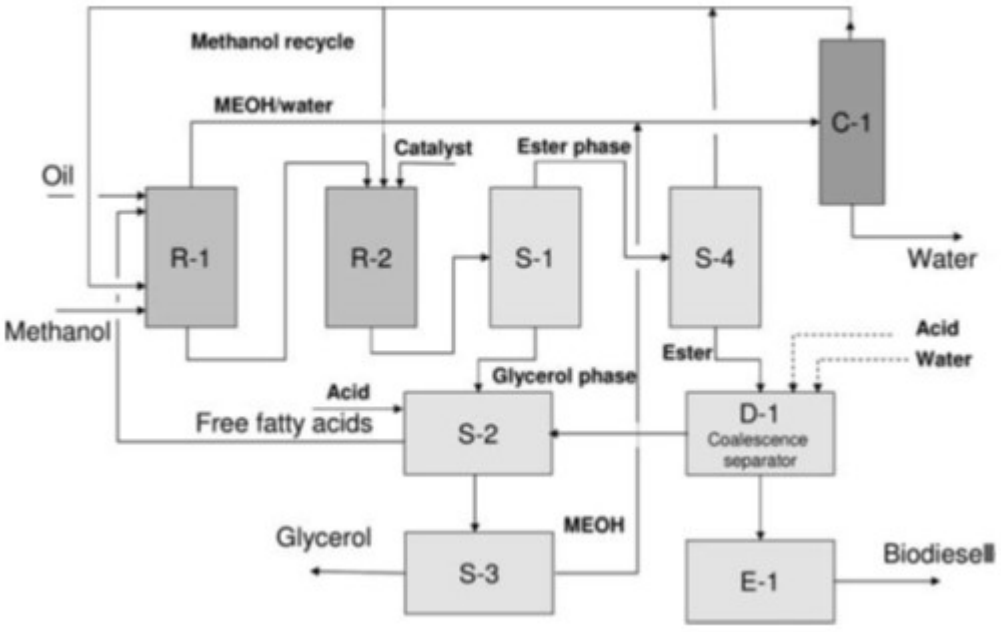
Some groups use a two-step reaction, with glycerol removal between steps, to increase the final reaction extent to 95+ percent. Higher temperatures and higher alcohol:oil ratios also can enhance the percent completion. Typical reaction times range from 20 minutes to more than one hour.

A popular variation of the batch process is the use of continuous stirred tank reactors (CSTRs) in the series. The CSTRs can be varied in volume to allow for a longer residence time in CSTR 1 to achieve a greater extent of reaction. After the initial product glycerol is decanted, the reaction in CSTR 2 is rather rapid, with 98+ completion not uncommon. An essential element in the design of a CSTR is sufficient mixing input to ensure that the composition throughout the reactor is essentially constant. This has the effect of increasing the dispersion of glycerol product in the ester phase. The result is that the time required for phase separation is extended.

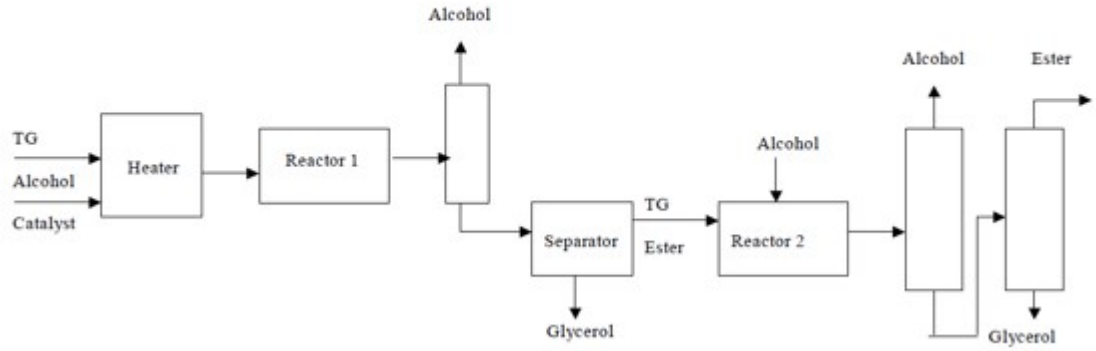
Batch Process Flow



Continuous Process Flow



Continuous Process Systems



Purification of Reaction Products

The mixture of fatty acids methyl esters (FAME) obtained from the transesterification reaction must be purified to comply with established quality standards for biodiesel. Therefore, FAME must be washed, neutralized and dried. Successive washing steps with water remove the remains of methanol, catalyst and glycerin, since these contaminants are water-soluble. Care must be taken to avoid the formation of emulsions during the washing steps, since they would reduce the efficiency of the process.

The first washing step is carried out with acidified water, to neutralize the mixture of esters. Then, two additional washing steps are made with water only. Finally, the traces of water must be eliminated by a drying step. After drying, the purified product is ready for characterization as biodiesel according to international standards.

Biodiesel vs. Renewable Diesel

Renewable diesel is another alternate fuel used in compression-ignition engines and is produced from some of the same renewable feedstocks as biodiesel. However, the way that these feedstocks are processed into renewable diesel is considerably different than biodiesel.

As discussed above, biodiesel is primarily made through transesterification to produce fatty acid methyl esters. Renewable diesel is produced by a process called hydroprocessing or hydrotreating, indicating a reaction with hydrogen.

Hydroprocessing produces chemicals identical to some of the compounds found in conventional diesel fuel. Like biodiesel, renewable diesel has very low sulfur content, which is advantageous environmentally. Renewable diesel typically has a very high cetane number and can be made to meet a range of cloud point requirements.

Biodiesel Is a Low-Carbon-Intensity Fuel and Reduces Greenhouse Gas Emissions

Carbon intensity refers to the amount of greenhouse gases emitted per unit of energy consumed, usually stated in grams of CO2 equivalent per megajoule (CO2eq/MJ). The carbon intensity of petroleum-based diesel fuels is typically around 95 g CO2eq/MJ.
Biodiesel carbon intensity depends on feedstock used but ranges from around 18 g CO2eq/MJ for waste cooking oil to 21 g CO2eq/MJ for soybean oil (or 30 g CO2eq/MJ when including indirect land use change effects).

Because of biodiesel's lower carbon intensity, when biodiesel displaces petroleum in any application, it significantly reduces life cycle greenhouse gas emissions. These life cycle analysis results show greenhouse gas emissions for soy B100 are 67% to 77% lower than those from petroleum diesel.

Biodiesel Reduces Soot Emissions

Because biodiesel contains approximately 11 wt% oxygen (i.e., an oxygenate), when it is blended into petroleum fuels it will dilute certain compounds that have a high soot (e.g., particulate matter) formation tendency and enhance combustion, thereby reducing particulate emissions. This is a major benefit for pre-2010 model year on-road engines and for many off-road engines not equipped with diesel particle filters. These reductions are greater for higher biodiesel blend levels, but also depend on engine design, calibration, and operating conditions. Biodiesel use in home heating oil systems and boilers can reduce soot by as much as 60% for B100 and roughly 10% for B20.

Biodiesel is a commercially available, lower-carbon-intensity fuel for use in diesel engines, boilers, and home heating oil systems. It can directly replace or be blended with distillate and residual fuel oils, like diesel fuel or heating oil.

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The Crude to Chemicals Refineries will Disrupt the Refining Business?

Dr. Marcio Wagner da Silva

Introduction and Context

The current scenario presents great challenges to the crude oil refining industry, prices volatility of raw material, pressure from society to reduce environmental impacts and refining margins increasingly lower. The newest threat to refiners is the reduction of the consumer market, in the last years became common, news about countries that intend to reduce or ban the production of vehicles powered by fossil fuels in the middle term, mainly in the European market. Despite the recent forecasts, the transportation fuels demand is still the main revenues driver to the downstream industry, but as presented in Figure 1, there is a significant trend of reduction in the transportation fuels consumption, especially gasoline.

According to Figure 1, a growing demand for petrochemicals is while the transportation fuels tend to present falling consumption, in the gasoline case is expected a retraction in the market around 1,7 %. Still according to Wood Mackenzie data, presented in Figure 2, due to the higher added value, the most integrated refiners tend to achieve higher refining margins than the conventional refiners which keep the operations focused on transportation fuels.

NCM = Net Cash Margins

The improvement in fuel efficiency, growing market of electric vehicles tends to decline the participation of transportation fuels in the global crude oil demand. New technologies like additive manufacturing (3D printing) have the potential to produce great impact to the transportation demands, leading to even more impact over the transportation fuels demand. Furthermore, the higher availability of lighter crude oils favors the oversupply of lighter derivatives that facilitate the production of petrochemicals against transportation fuels as well as the higher added value of petrochemicals in comparison with fuels. According to Figure 3, the demand for petrochemicals tends to rise in the next years and can be an attractive way to refiners keep his protagonism in the market.

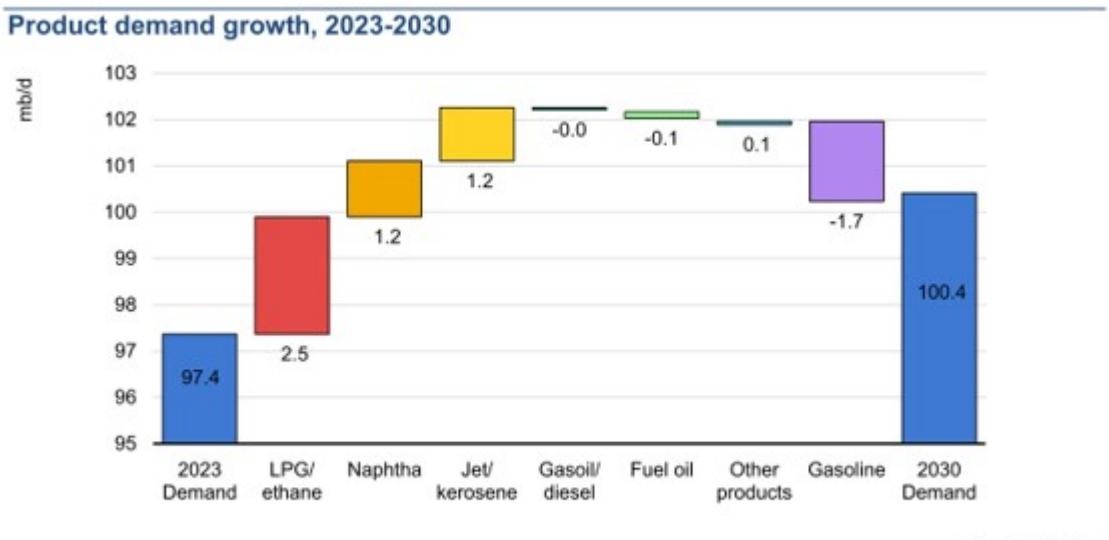

Figure 1 – Global Oil Demand by Derivative (International Energy Agency, 2024)

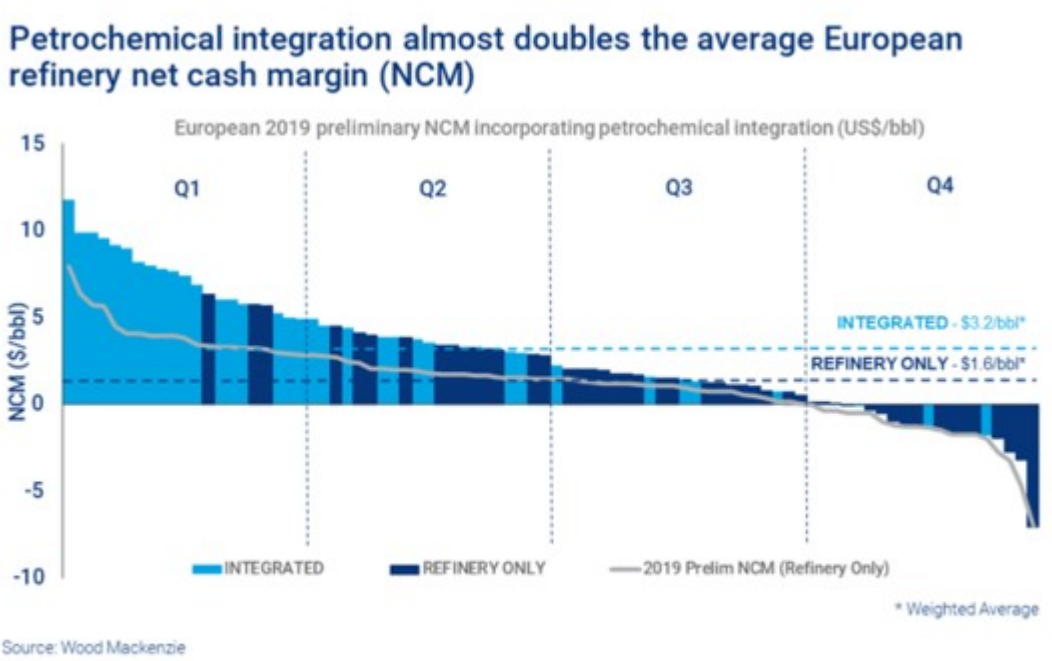

Figure 2 – Refining Margins to Integrated and Non-Integrated Refining Hardware (Wood Mackenzie, 2020)

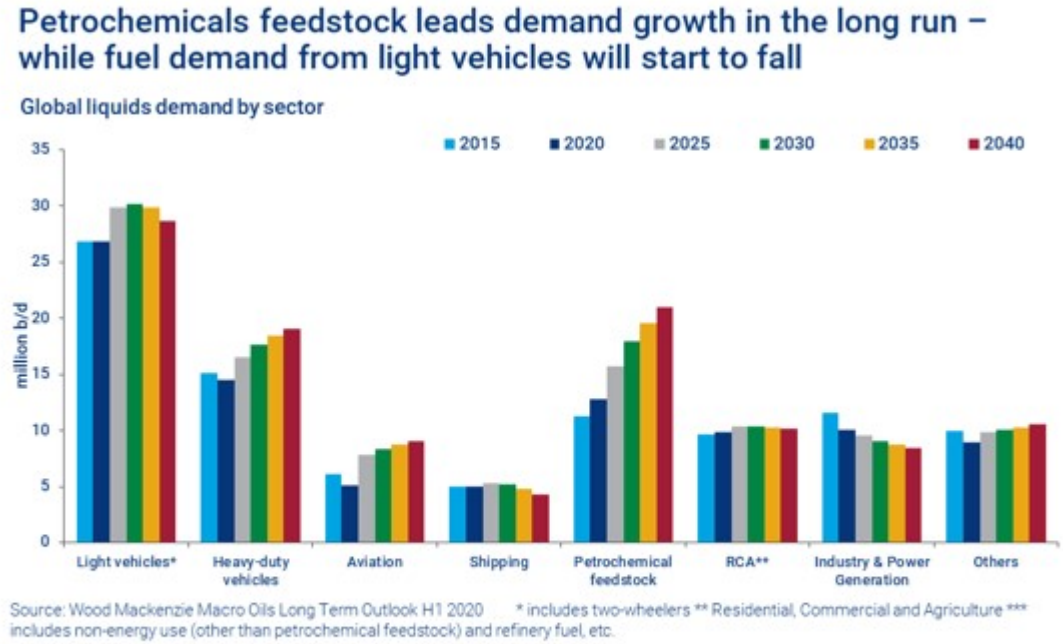

Figure 3 – Growing Trend in the Demand by Petrochemical Intermediates (Wood Mackenzie, 2020)

According to data presented in Figure 3, a significant growth in the market of petrochemical intermediates is expected, and a refining hardware capable of maximizing the yield of these derivatives can offer significant competitive advantage through closer integration with petrochemical assets and higher value addition to processed crude oil. Taking as example in the North American Market, it's possible to observe the falling demand by transportation fuels, as presented in Figure 4.

Another deep change in the downstream sector that reinforces the necessity of a high conversion refining hardware is the IMO 2020. Restrictive regulations like IMO 2020 raised, even more, the pressure over refiners with low bottom barrel conversion capacity once requires higher capacity to add value to residual streams, especially related to sulfur content that was reduced from 3,5 % (in mass) to 0,5 %. Refiners with easy access to low sulfur crude oils present relative competitive

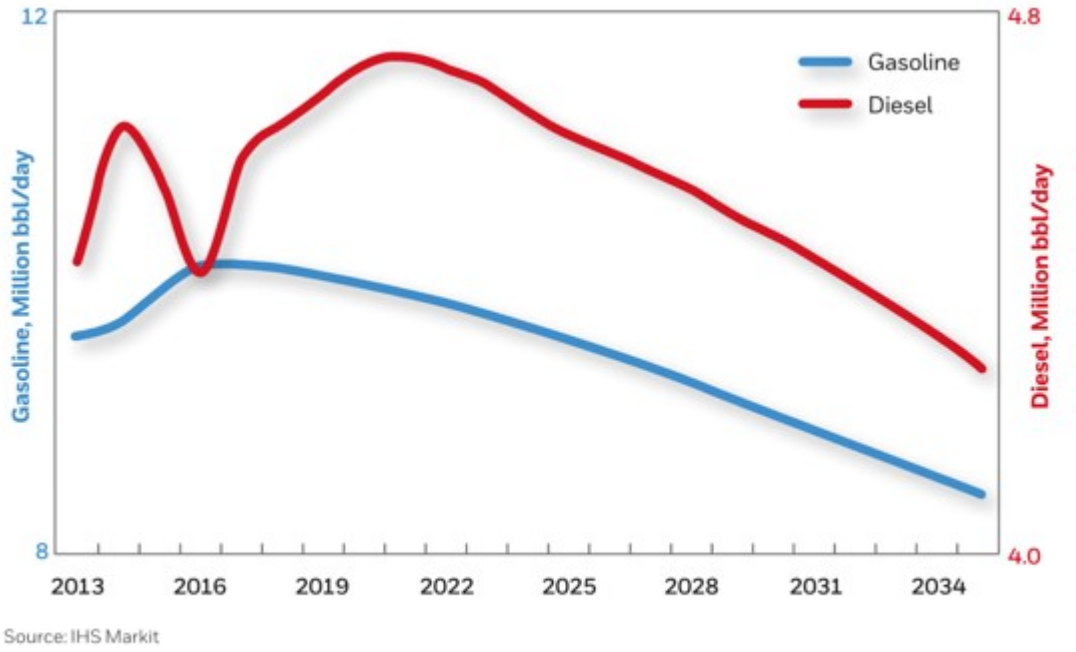

Figure 4 – Transportation Fuels Demand for the North American Market (UOP Company, 2021)

advantage in this scenario. These players can rely on relatively low-cost residue upgrading technologies to produce the new marine fuel oil (Bunker) as carbon rejection technologies (Solvent Deasphalting, Delayed Coking, etc.), but they are the minority in the market. The most part of the players need to look for sources of low sulfur crudes, which present higher costs, putting under pressure their refining margins or looking for deep bottom barrel conversion technologies to ensure more value addition to processed crude oils and avoid to loss competitiveness in the downstream market. For these refiners, deepest residue upgrading like hydrocracking technologies can offer great operational flexibility, despite the high capital spending. In this scenario, with necessity to higher value addition to bottom barrel stream and growing market of petrochemicals, refiners with adequate bottom barrel conversion capacity can achieve great competitive advantage in the downstream industry.

Based on description above it's possible to apply the article published by W. Chan Kim and Renée Mauborge called "Blue Ocean Strategy" in Harvard Business Review, to classify the competitive markets in the downstream industry. In this article the authors define the conventional market as a red ocean where the players tend to compete in the existing market focusing on defeating competitors through the exploration of existing demand, leading to low differentiation and low profitability. The blue ocean is characterized by looking for space in creating and developing new demands and reaching differentiation. This model can be applied (with some specificities once is a commodity market) to the downstream industry, considering the traditional transportation fuels refineries and the petrochemical sector.

Due his characteristics, the transportation fuels market can be imagined like the red ocean, where the margins tend to be low and under high competition between the players with low differentiation capacity. On the other side the petrochemicals sector can be faced like the blue ocean where few players are able to meet the market in competitive conditions, higher refining margins, and significant differentiation in relation to refiners dedicated to transportation fuels market. Figure 5 presents the basic concept of blue ocean strategy in comparison with the traditional red ocean where the players fight to market share with low margins.

As presented above, the market forecasts indicate that the refiners able to maximize petrochemicals against transportation fuels can achieve highlighted economic performance in short term, in this sense, the crude oil to chemicals technologies can offer even more competitive advantage to the refiners with capacity of capital investment.

Can be difficult to some people to understand the term "differentiation" in the downstream industry once this is a market that deal with commodities, but the differentiation here is related to the capacity to reach more added

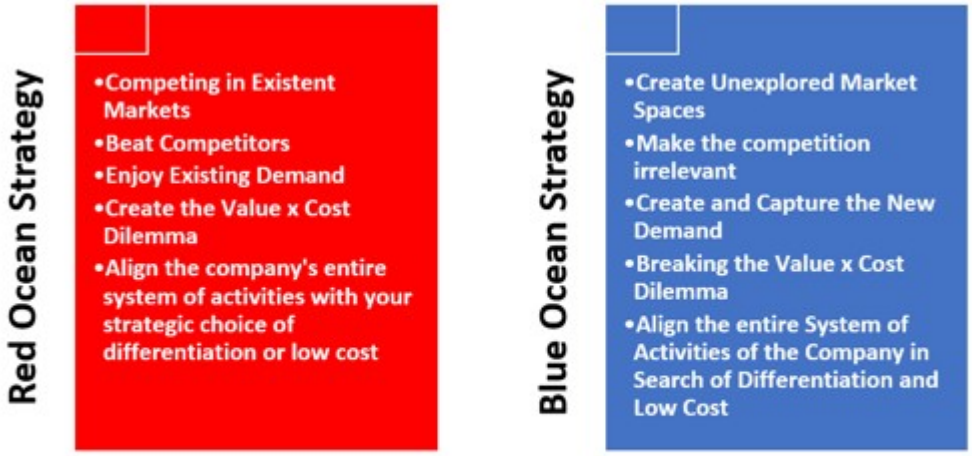

Figure 5 – Differences between Blue and Red Ocean Strategies (KIM & MAUBORGNE, 2004)

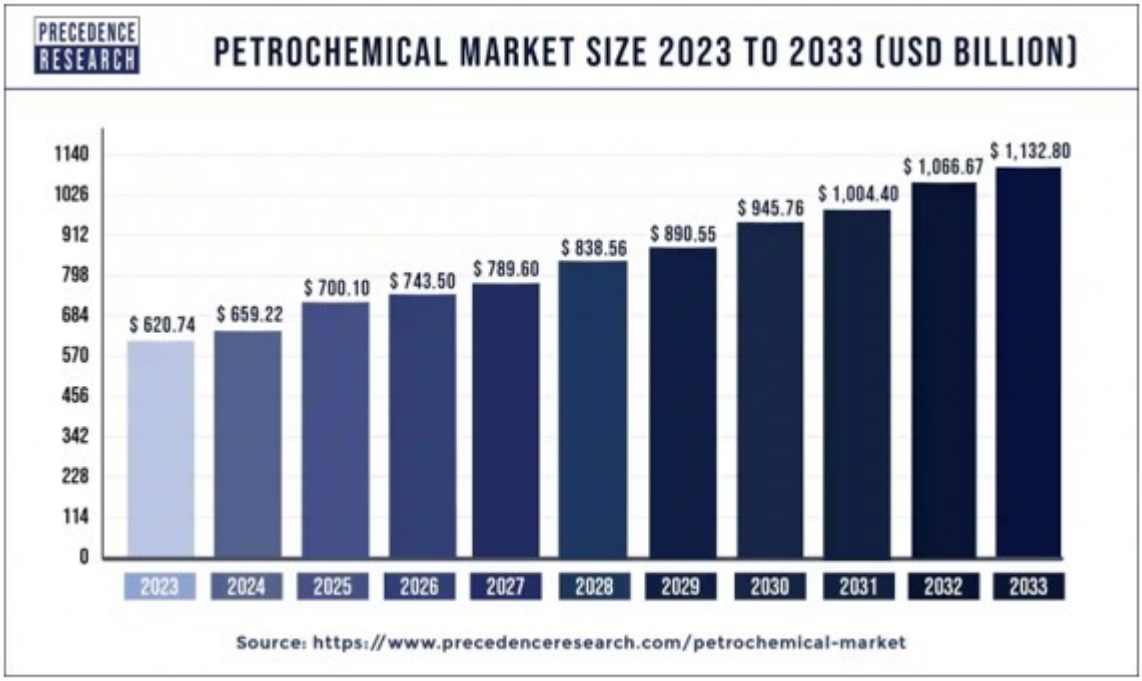

Figure 6 – Petrochemical Market Size Forecast 2023-2033 (Precedence Research, 2024)

value to the processed crude oil and as presented above, nowadays this is translated in the capacity to maximize the petrochemicals yield, creating differentiation between integrated and non-integrated players.

Considering 2023 as the base year, the petrochemical market size reached a total value of USD 620,74 billion with an expected compound annual growth rate (CAGR) of 6,20 % between 2024 and 2033 as presented in Figure 6.

Based on these data, the petrochemical market size can reach a total value of close USD 1.132,80 billion in 2033, reinforcing the attractiveness of the petrochemical market for the refiners under a scenario where the transportation fuels show in contraction demand and hostile scenario due to the necessity to reduce the carbon intensity of the energetic matrix.

Considering just the aromatics solvent market (Benzene, Toluene, and Xylenes) the CAGR expected between 2021 and 2030 is 4,8 % leading the aromatics solvent market size reach USD 8,1 billion in 2030 still according to Precedence Research data.

Considering exclusively the propylene market, the forecasts are even more encouraging for investments in on purpose propylene production routes. Figure 7 presents the

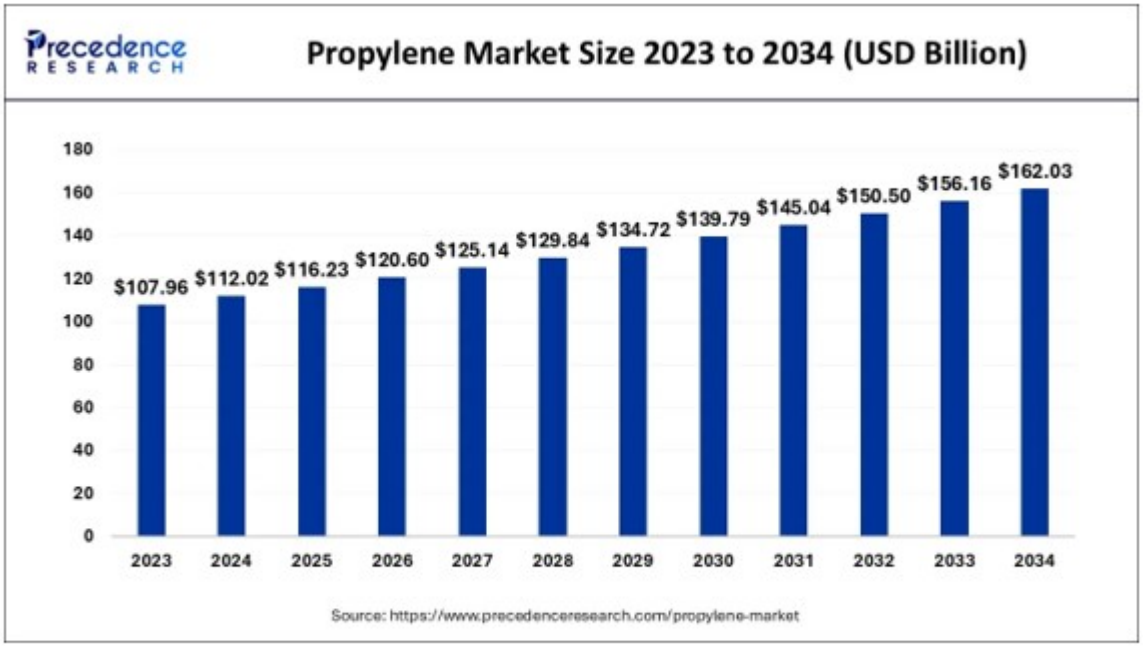

Figure 7 – Evolution of Propylene Market Size for the next years (Precedence Research, 2024)

projection to propylene market size for the next years.

According to Figure 7, the propylene market can reach higher than 160 billion USA dollars in 2034 with an annual rate of 3,76 % with Asia being the bigger market as expected.

Synergies between Refining and Petrochemical Assets – Petrochemical Integration

The focus of the closer integration between refining and petrochemical industries is to promote and seize the synergies existing opportunities between both downstream sectors to generate value to the whole crude oil production chain. Table 1 presents the main characteristics of the refining and petrochemical industry and the synergies potential.

As aforementioned, the petrochemical industry has been growing at considerably higher rates when compared with the transportation fuels market in the last years, additionally, represents a noblest destiny and less environmentally aggressive to crude oil derivatives. The technological bases of the refining and petrochemical industries are similar, which leads to possibilities of synergies capable of reducing operational costs and adding value to derivatives produced in the refineries.

Figure 8 presents a block diagram that shows some integration possibilities between refining processes and the petrochemical industry.

Table 1 – Refining and Petrochemical Industry Characteristics

Refining Industry	Petrochemical Industry
Large Feedstock Flexibility	Raw Material from Naphtha/NGL
High Capacities	Higher Operation Margins
Self Sufficient in Power/Steam	High Electricity Consumption
High Hydrogen Consumption	High Availability of Hydrogen
Streams with low added Value (Unsaturated Gases & C2)	Streams with Low Added Value (Heavy Aromatics, Pyrolysis Gasoline, C4's)
Strict Regulations (Benzene in Gasoline, etc.)	Strict Specifications (Hard Separation Processes)
Transportation Fuels Demand in Declining at Global Level	High Demand Products

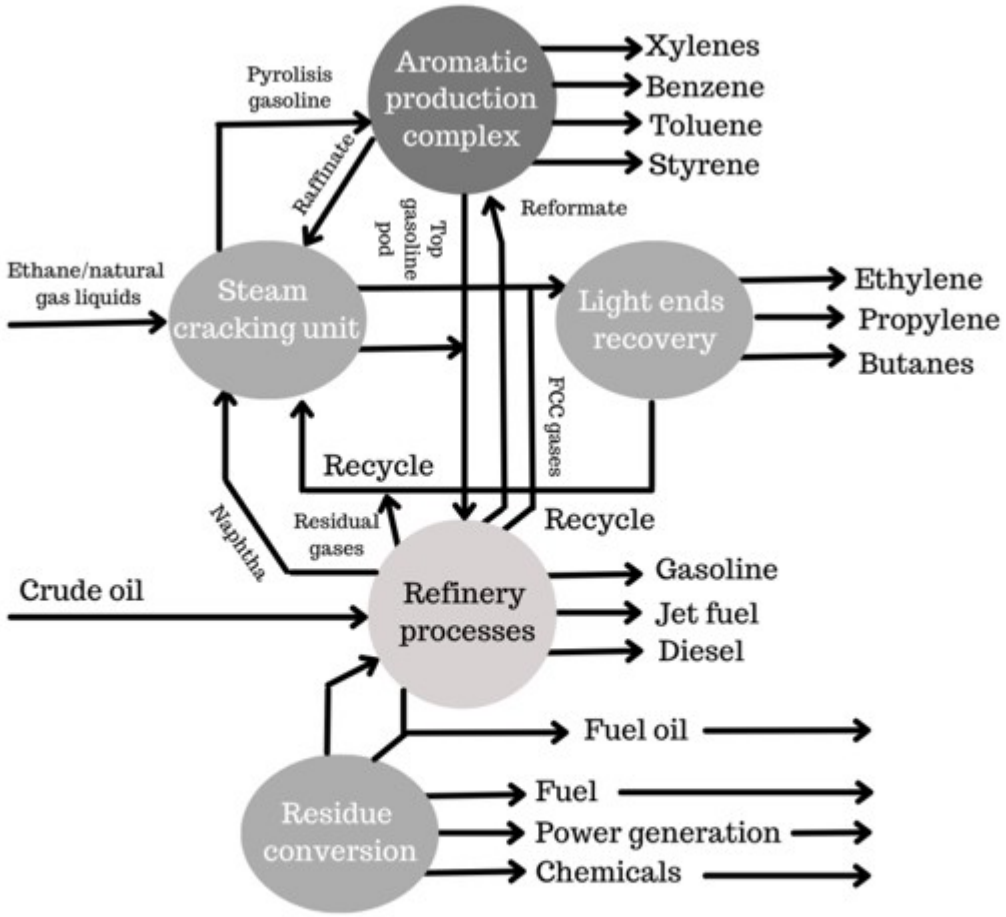

Figure 8 – Synergies between Refining and Petrochemical Processes

Process streams considered with low added value to refiners like fuel gas (C2) are attractive raw materials to the petrochemical industry, as well as streams considered residual to petrochemical industries (butanes, pyrolisis gasoline, and heavy aromatics) can be applied to refiners to produce high quality transportation fuels, this can help the refining industry meet the environmental and quality regulations to derivatives.

The integration potential and the synergy among the processes rely on the refining scheme adopted by the refinery and the consumer market. Process units such as Fluid Catalytic Cracking (FCC) and Catalytic Reforming can be optimized to produce petrochemical intermediates to the detriment of streams that will be incorporated to fuels pool. In the case of FCC, installation of units dedicated to producing petrochemical intermediates, called petrochemical FCC, aims to reduce to the minimum the generation of streams to produce transportation fuels, however, the capital investment is high once the severity of the process requires the use of material with noblest metallurgical characteristics.

The IHS Markit Company proposed a classification of the petrochemical integration grades, as presented in Figure 9.

According to the classification proposed, the crude to chemicals refineries is considered the maximum level of petrochemical integration where the processed crude oil is totally converted into petrochemical intermediates like ethylene, propylene, and BTX. Considering the current scenario of the downstream industry, the crude to chemicals refineries can create the necessary differentiation to allow the players to reach the Blue Ocean Strategy.

The Crude Oil to Chemicals Refining Assets

Due to the increasing market and higher added value as well as the trend of reduction in transportation fuels demand, some refiners and technology developers have dedicated their efforts to develop crude to chemicals refining assets. One of the big players that have been invested in this alternative is the Saudi Aramco Company, the concept is based on the direct conversion of crude oil to

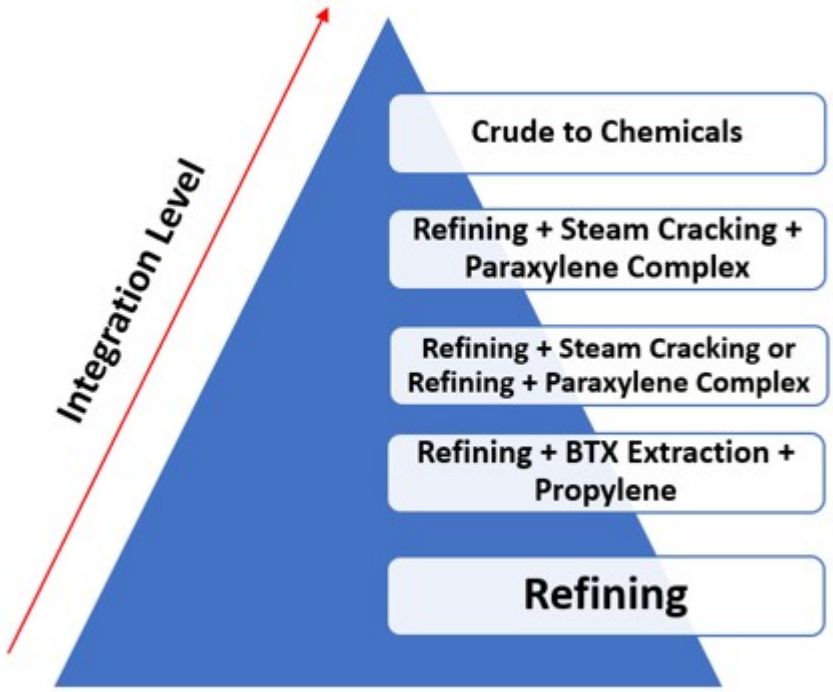

Figure 9 – Petrochemical Integration Levels (IHS Markit, 2018)

petrochemical intermediates as presented in Figure 10.

The process presented in Figure 8 is based on the quality of the crude oil and deep conversion technologies like High Severity or petrochemical FCC units and deep hydrocracking technologies. The processed crude oil is light with low residual carbon that is a common characteristic in the Middle East crude oils, the processing scheme involves deep catalytic conversion aiming to reach maximum conversion to light olefins. In this refining configuration, the petrochemical FCC units have a key role to ensure high added value to the processed crude oil.

An example of FCC technology developed to maximize the production of petrochemical intermediates is the PetroFCC™ process by

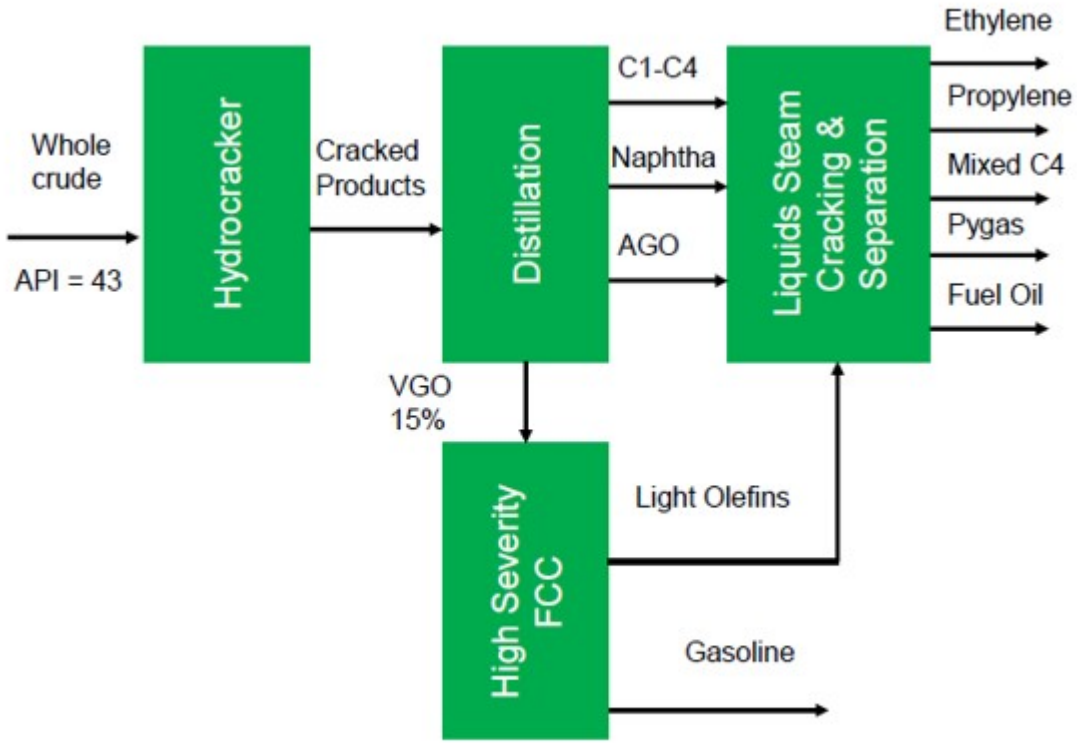

Figure 10 – Saudi Aramco Crude Oil to Chemicals Concept (IHS Markit, 2017)

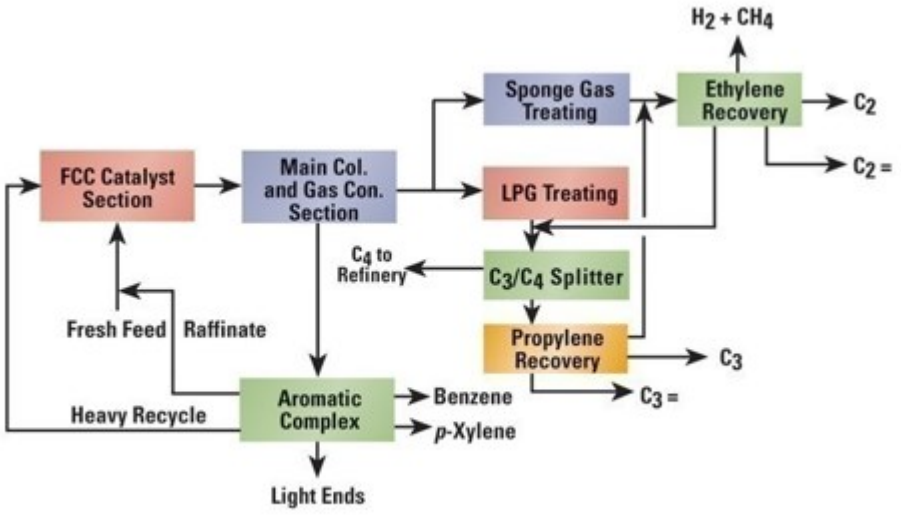

Figure 11 – PetroFCC™ Process Technology by UOP Company.

UOP Company, this process combines a petrochemical FCC and separation processes optimized to produce raw materials to the petrochemical process plants, as presented in Figure 9. Other available technologies are the HS -FCC™ process commercialized by Axens Company, and INDMAX™ process licensed by Lummus Company. The basic process flow diagram for HS-FCC™ technology is presented in Figure 11.

It's important to consider that the technology presented in Figure 11 is based on Petrochemical FCC units that present especial design due to the severe operating conditions.

To petrochemical FCC units, the reaction temperature reaches 600 oC and higher catalyst circulation rate raises the gases production, which requires a scaling up of gas separation section. The higher thermal demand makes advantageous operates the catalyst regenerator advantageous, leading to the necessity of installation a catalyst cooler system.

The installation of petrochemical catalytic cracking units requires a deep economic study considering the high capital investment and higher operational costs; however, some forecasts indicate growth of 4,0 % per year to the market of petrochemical intermediates until 2025. In this scenario the capital investment aiming to raise the market share in the petrochemical sector can be attractive, allowing then a favorable competitive positioning to the refiner, through the maximization of petrochemical intermediates. Figure 12 presents a block diagram showing a case study demonstrating how the petrochemical FCC unit, in this case the INDMAX™ technology by Lummus Company, can maximize the yield of petrochemicals in the refining hardware. Another technology dedicated to maximizing olefins from residue is the R2P™ process, developed by Axens.

In refining hardware with conventional FCC units, further than the higher temperature and catalyst circulation rates, it's possible to apply the addition of catalysts additives like the zeolitic material ZSM-5 that can raise the olefins yield close to 9,0% in some cases when compared with the original catalyst. This alternative raises the operational costs, however, as aforementioned can be economically attractive considering the petrochemical market forecasts.

Installation of catalyst cooler system raises the process unit profitability through the total conversion enhancement and selectivity to noblest products as propylene and naphtha against gases and coke production. The catalyst cooler is necessary when the unit is designed to operate under total combustion mode due to the higher heat release rate as presented below.

$C + ½\ O2 \rightarrow CO$ (Partial Combustion) $\Delta H = -27$ kcal/mol

$C + O2 \rightarrow CO2$ (Total Combustion) $\Delta H = -94$ kcal/mol

In this case, the temperature of the regeneration vessel can reach values close to 760 oC, leading to higher risks of catalyst damage which is minimized through catalyst cooler installation. The option by the total combustion mode needs to consider the refinery thermal balance, once, in this case, will not have the possibility to produce steam in the CO boiler, furthermore, the higher temperature in the regenerator requires materials with noblest metallurgy, this raises significantly the installation costs of these units which can be prohibitive to some refiners with restricted capital access.

Another key to refining technology to crude oil to chemicals refineries is the hydrocraking

units. Despite the high performance, the fixed bed hydrocracking technologies can be economically effective to treat crude oils directly cue to the possibility of short operating lifecycle. Technologies that use ebullated bed reactors and continuum catalyst replacement allow higher campaign period and higher conversion rates, among these technologies the most known are the H-Oil and Hyvahl™ technologies developed by Axens Company, the LC-Fining Process by Chevron-Lummus, and the Hycon™ process by Shell Global Solutions. These reactors operate at temperatures above 450 oC and pressures to 250 bar. Figure 13 presents a typical process flow diagram for a LC-Fining™ process unit, developed by Chevron Lummus Company while the H-Oil™ process by Axens Company is presented in Figure 14.

Catalysts applied in hydrocracking processes can be amorphous (alumina and silica-alumina) and crystalline (zeolites) and have bifunctional characteristics, once the cracking reactions (in the acid sites) and hydrogenation (in the metals sites) occur simultaneously.

An improvement in relation to ebullated bed technologies is the slurry phase reactors, which can achieve conversions higher than 95 %. In this case, the main available technologies are the HDH™ process

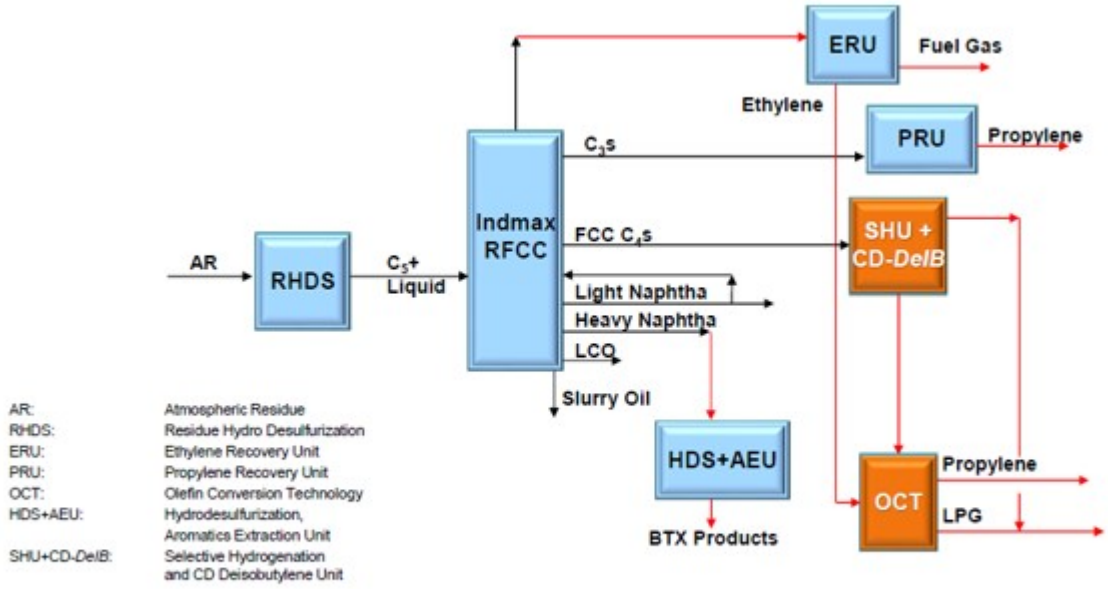

Figure 12 – Olefins Maximization in the Refining Hardware with INDMAX™ FCC Technology by Chevron Lummus Global Company (SANIN, A.K., 2017)

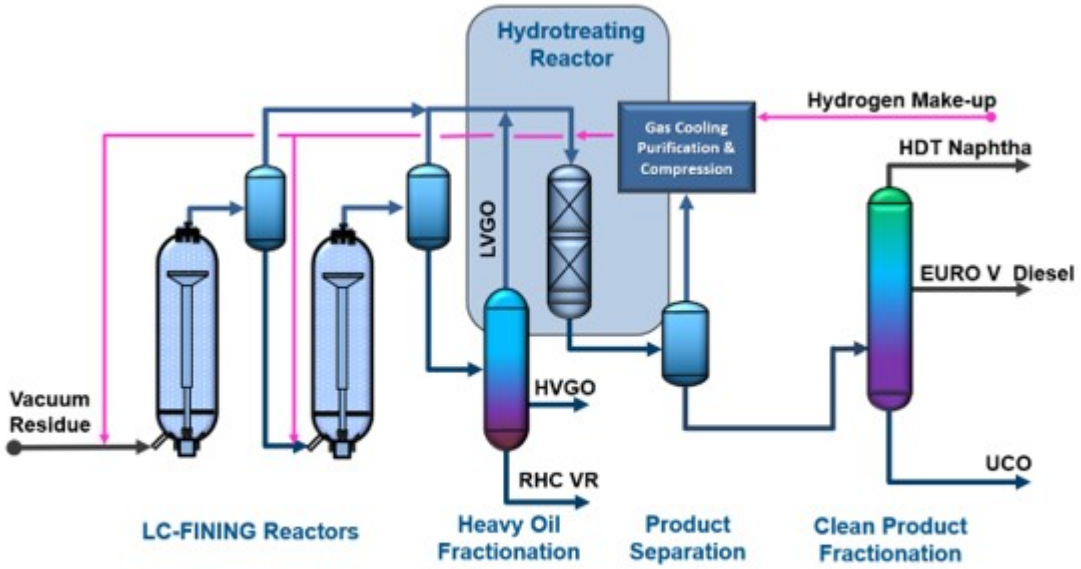

Figure 13 – Process Flow Diagram for LC-Fining™ Technology by CLG Company (MUKHERJEE & GILLIS, 2018)

(Hydrocracking-Distillation-Hydrotreatment), developed by PDVSA-Intevep, VEBA-Combicracking Process (VCC)™ commercialized by KBR Company, the EST™ process (Eni Slurry Technology) developed by Italian state oil company ENI, and the Uniflex™ technology developed by UOP Company. Figure 15 presents a basic process flow diagram for the VCC™ technology by KBR Company.

In the slurry phase hydrocracking units, the catalysts in injected with the feedstock and activated in situ while the reactions are carried out in slurry phase reactors, minimizing the reactivation issue, and ensuring higher conversions and operating lifecycle. Figure 16 presents a basic process flow diagram for the Uniflex™ slurry hydrocracking technology by UOP Company.

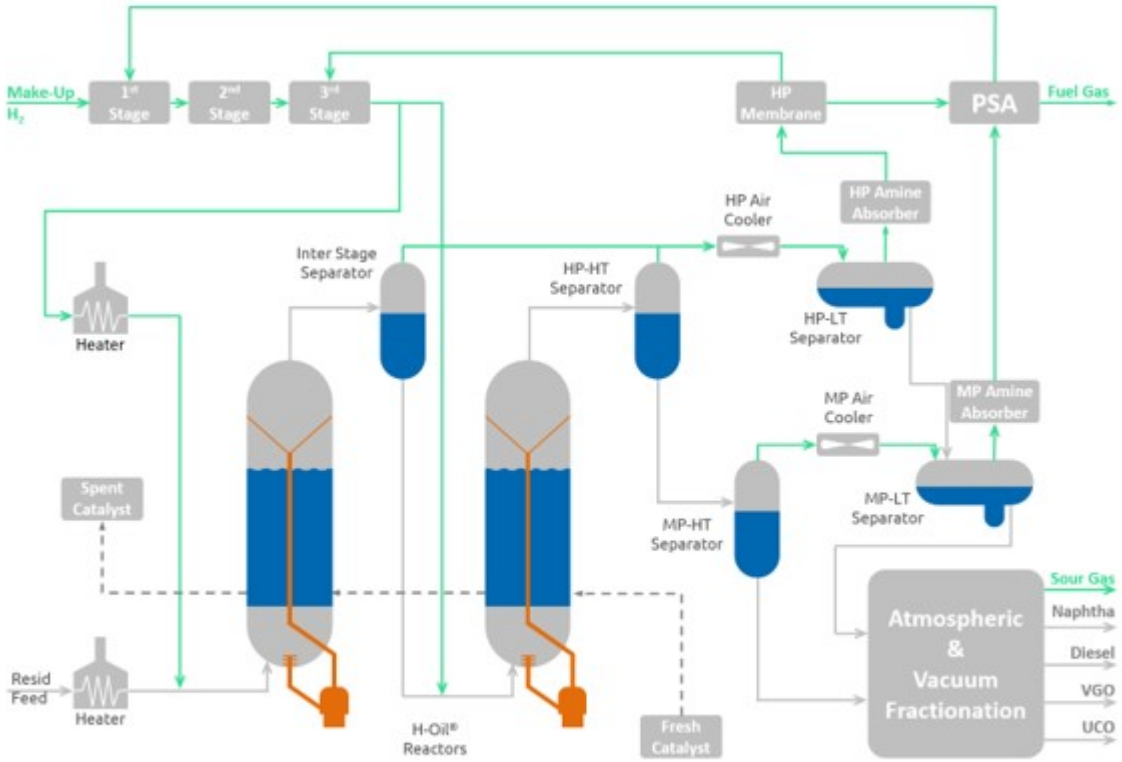

Figure 14 – Process Flow Diagram for H-Oil™ Process by Axens Company (FRECON et. al, 2019)

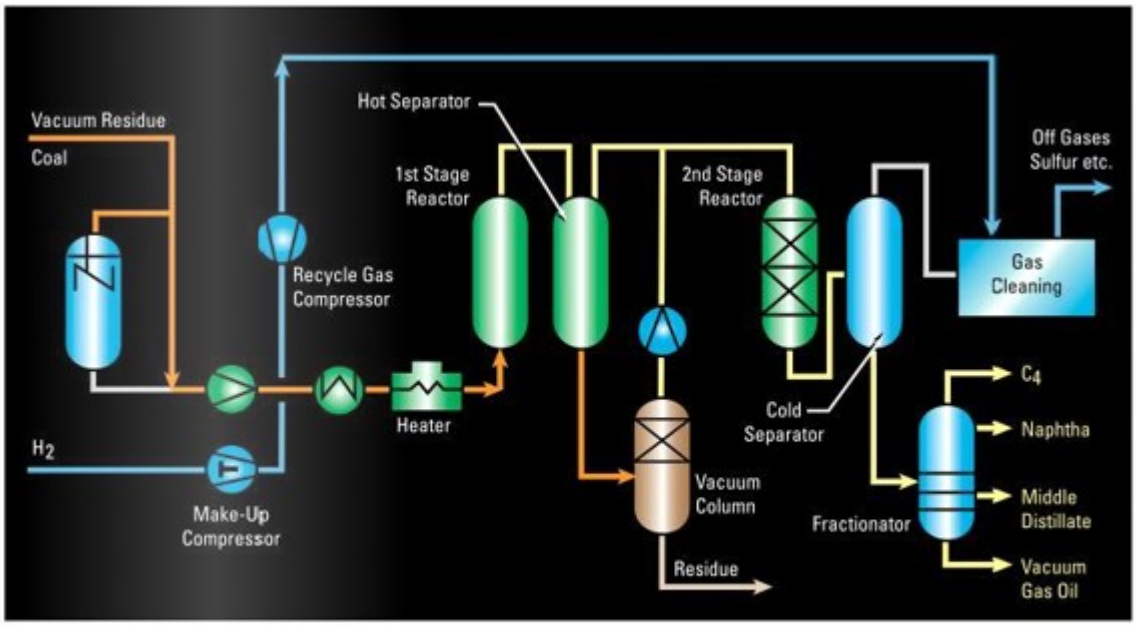

Figure 15 – Basic Process Arrangement for VCC™ Slurry Hydrocracking by KBR Company (KBR Company, 2019)

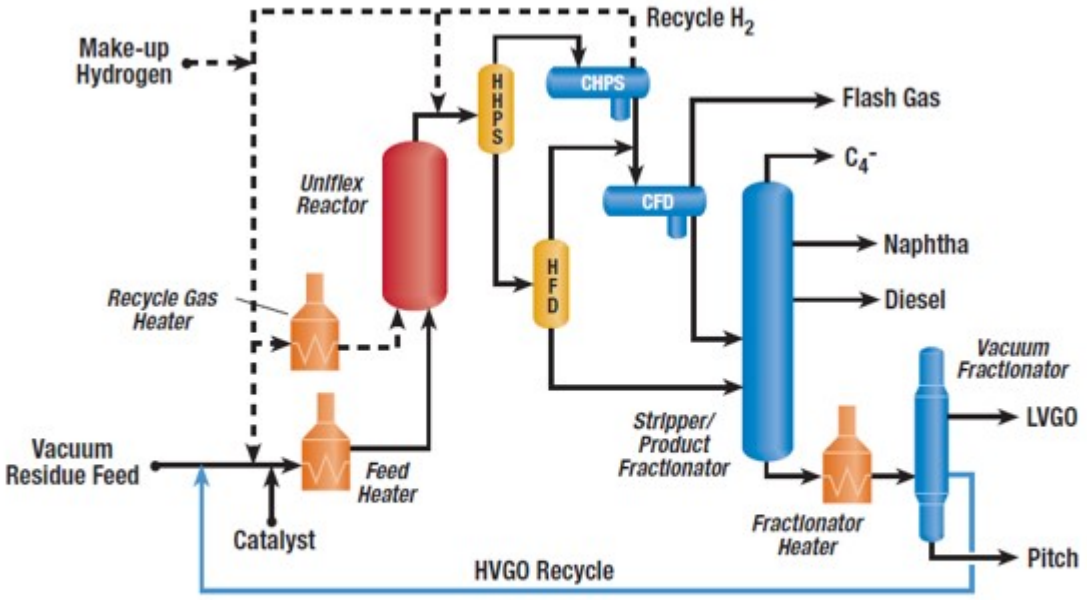

Figure 16 – Process Flow Diagram for Uniflex™ Slurry Phase Hydrocracking Technology by UOP Company (UOP Company, 2019).

Other commercial technologies to slurry hydrocracking process are the LC-Slurry™ technology developed by Chevron Lummus Company and the Microcat-RC™ process by Exxon Mobil Company.

For this side, the Steam cracking process has a fundamental role in the petrochemical industry, nowadays the most part of light olefins light ethylene and propylene are produced through steam cracking route. The steam cracking consists of a thermal cracking process that can use gas or naphtha to produce olefins.

The naphtha to steam cracking is composed basically of straight run naphtha from crude oil distillation units, normally to meet the requirements as petrochemical naphtha the stream needs to present high paraffin content (higher than 66 %). Figure 17 presents a typical steam cracking unit applying naphtha as raw material to produce olefins.

Due to his relevance, great technology developers have dedicated their efforts to improve steam cracking technologies over the years, especially related to steam cracking furnaces. Companies like Stone & Webster, Lummus, KBR, Linde, and Technip develop technologies to steam cracking process. One of the most known steam cracking technologies is the SRT™ process (Short Residence Time), developed by Lummus Company, that applies a reduce residence time to minimize the coking process and ensure higher operational lifecycle. Another commercial technology dedicated to optimizing the yield of ethylene is the SCORE™ technology developed by KBR and ExxonMobil Companies which combines a selective steam cracking furnace with high performance olefins recovery section.

The cracking reactions occur in the furnace tubes, the main concern and limitation to operating lifecycle of steam cracking units is the coke formation in the furnace tubes. The reactions are carried out under high temperatures, between 500 oC to 700 oC according to the characteristics of the feed (inlet temperature). For heavier feeds like gas oil, lower temperature is applied aiming to minimize the coke formation, the combination of high temperatures and low residence time are the main characteristic of the steam cracking process.

As quoted above, some technology developers are dedicating their efforts to develop commercial crude to chemicals refineries. Figure 18 presents the concept of crude to chemicals refining scheme by Chevron Lummus Company.

Another crude to chemicals refining arrangements is proposed by Chevon Lummus Company, applying the synergy of residue upgrading strategies to maximize the petrochemical intermediates production, Figure 19 presents a crude to chemicals arrangement relying on delayed coking unit.

Another great refining technology developers like UOP, Shell Global Solutions, ExxonMobil, Axens, and others are developing crude to

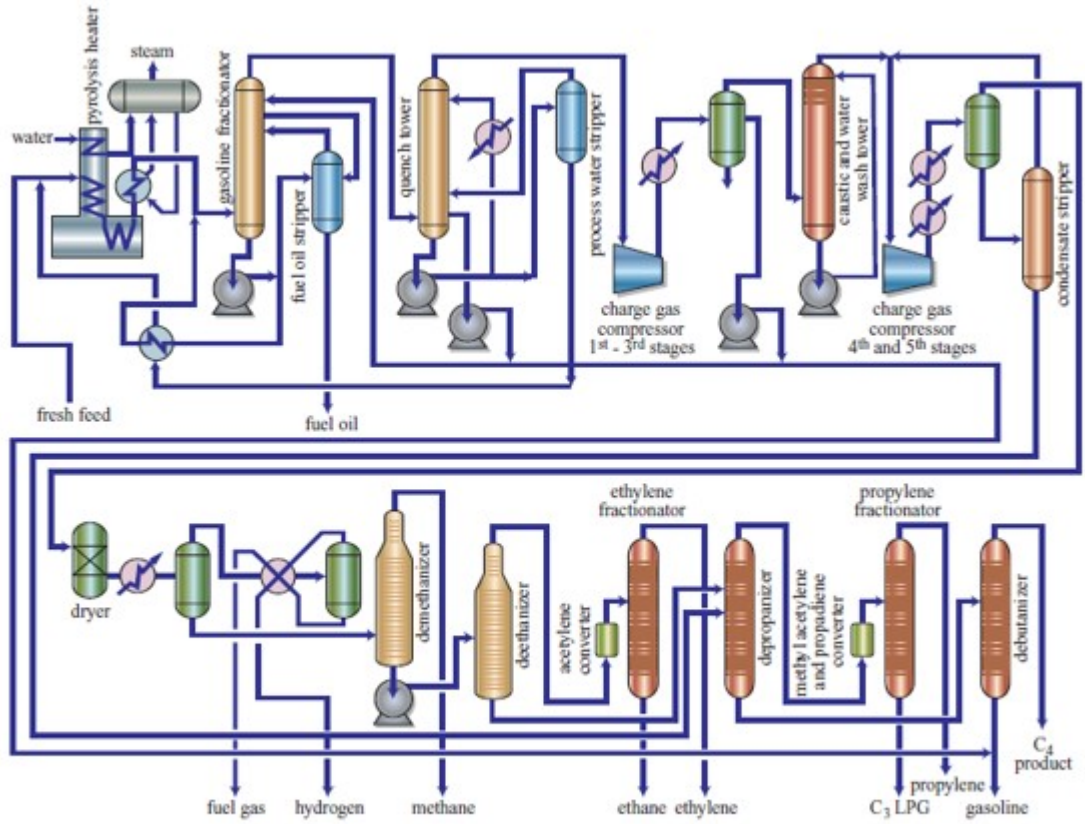

Figure 17 – Typical Naphtha Steam Cracking Unit (Encyclopedia of Hydrocarbons, 2006)

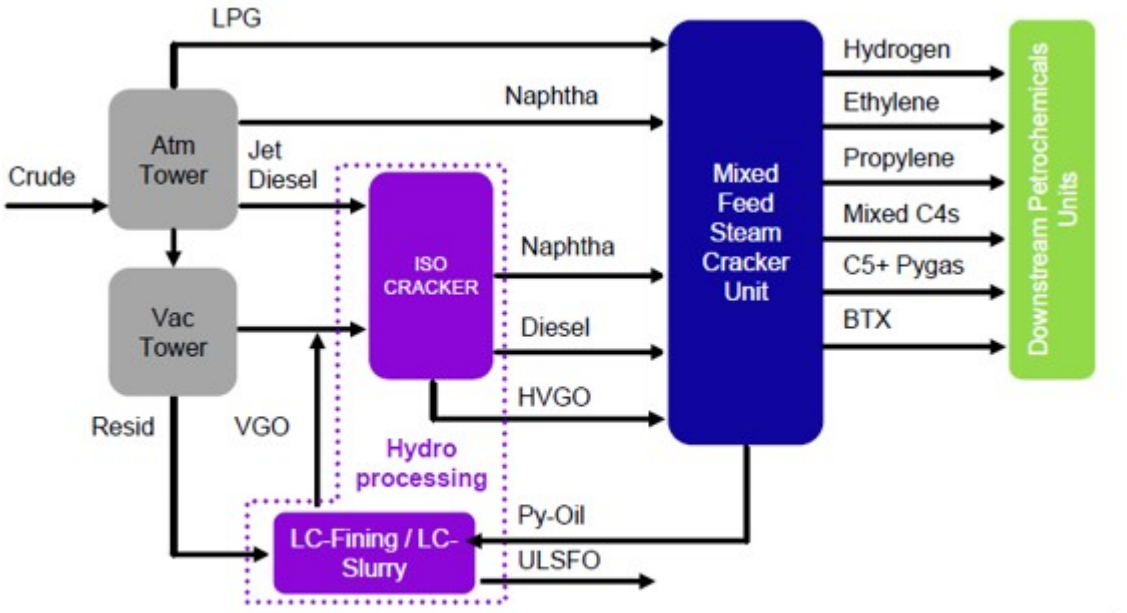

Figure 18 – Crude to Chemicals Concept by Chevron Lummus Company (Chevron Lummus Global Company, 2019)

chemicals technologies, reinforcing that this is a trend in the downstream market. Figure 20 presents a highly integrated refining configuration capable of converting crude oil to petrochemicals developed by UOP Company.

As presented in Figure 20, the production focus changes to the maximum adding value to the crude oil through the production of high added value petrochemical intermediates or chemicals to general purpose leading to a minimum production of fuels.

As aforementioned, big players as Saudi Aramco Company have been made great investments in COC technologies aiming to achieve even more integrated refineries and petrochemical plants, raising considerably his competitiveness in the downstream market. Major technology licensors like Axens, UOP, Lummus, Shell, ExxonMobil, etc. have been applied resources to develop technologies capable to allow a closer integration in the downstream sector aiming to allow refiners to extract the maximum added value

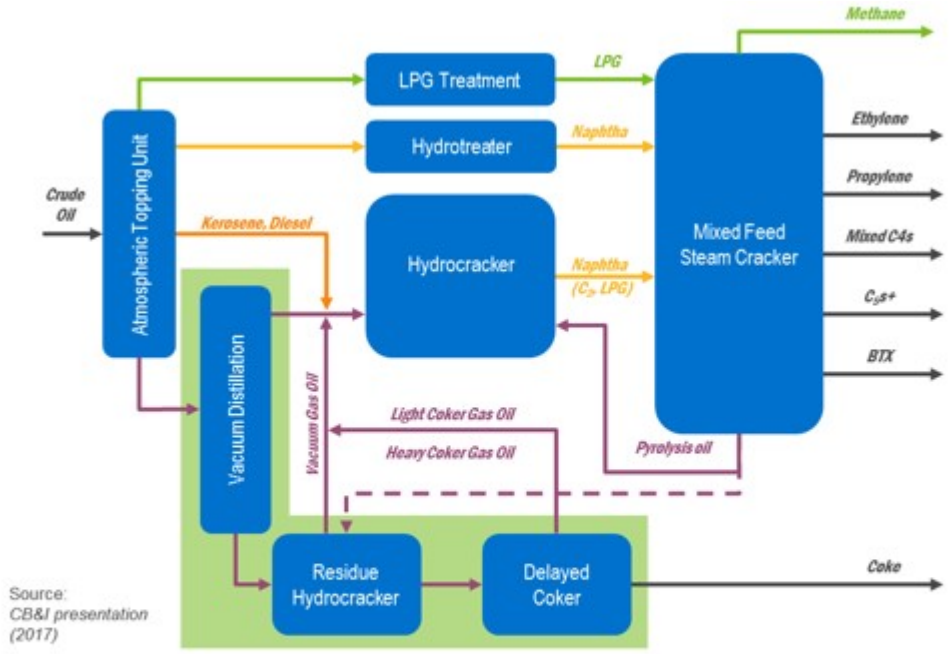

Figure 19 – Crude to Chemicals Concept by Chevron Lummus Company (Nexant Company, 2018)

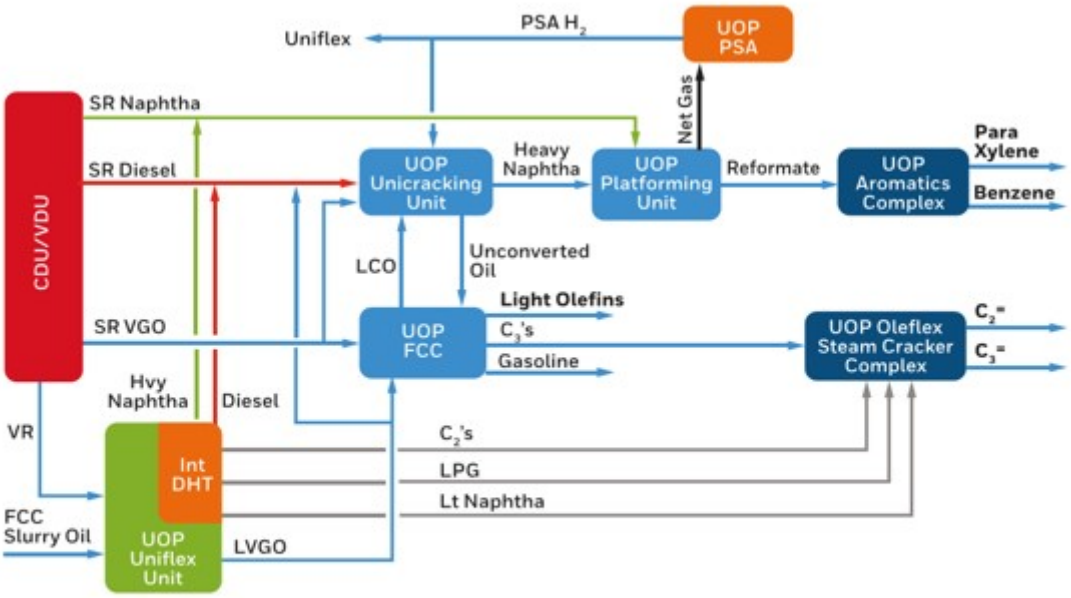

Figure 20 – Integrated Refining Configuration Based in Crude to Chemicals Concept by UOP Company.

from the processed crude oil, an increasing necessity in a scenario where the refining margins are under pressure.

Is expected that some of these capital investments was postponed due to the economic crisis provoked by the COVID-19 pandemic, but these data reinforce the trend in the market, it's interesting to quote that close to 64 % of the global crude to chemicals investments are made by Asian players. Considering just the petrochemical complexes focused on PX (Para Xylene), we have total capital investments around 87 US billion dollars presented in Figure 21.

Figure 22 presents a comparison between the petrochemicals yields of traditional refineries, a benchmark integrated refinery and crude to chemicals complexes, according to data from Wood Company.

Analyzing Figure 22 it's possible to note the higher added value reached in crude to chemicals refineries when compared even with highly integrated refineries. Figure 23 presents an example of how a crude to chemicals refineries can reach very high petrochemicals yield, in this case, considering the Hengli Petrochemical Complex in China.

It's interesting to quote the potential competitive imbalance of the downstream industry in the short term due to the growing demand for petrochemicals. Based on data from 2019 the total capital investments in crude to chemicals refineries is 300 billion US dollars and 64 % of this investment was made by Asian players, to reinforce this trend Figure 24 present a comparison between the relation of crude oil distillation capacity and the integrated refinery capacity for each continent.

Project	Refinery Capacity (MMt)	P-Xylene Capacity (MMt)	Ethylene Capacity (MMt)	Propylene Capacity (MMt)	Est. Chemical conversion/ bbl. of oil (%)	Investment ($bn)	Full line Operation
Hengli Petrochemical	20	4.3	1.5	1.0	42	11.4 (Excl. SC)	May 17, 2019
Zhejiang Petroleum and Chemical (ZPC) Phase 1	20	4.0	1.4	0.65	45	12	Dec 31. 2020
Hengyi (Brunei) PMB Refinery-Petrochem Phase 1	8	1.5	0.5	0.2	>40	3.45	Nov 3, 2019
Zhejiang Petroleum and Chemical (ZPC) Phase 2	20	4.8[a]	1.5	0.7	50[a]	12	Jan 12, 2022
Shenghong refinery and Integrated Petrochem	16	4.0[b]	1.4[c]	0.5	60[b]	9.6[c]	2022
Hengyi (Brunei) PMB Refinery-Petrochem Phase 2	14	2.0	1.5	0.7	>40	10	2022
Tangshan Xuyang (Risun)[d]	15	3.5	1.5	0.6	>50	8.5	**On Hold**
Shandong Yulong (Phase 1)[e]	20	4.0	3.0	1.2	> 50	20 (1st phase)	2024 (1st phase)
Total	**133**	**28.1**	**12.3**	**5.6**	--	**87**	--

a. ZPC/UOP press release Jan. 17, 2019 announced that Phase 2 configuration and technology will be changed from Phase 1.
b. Based on information obtained by IHSM from a visit to Shenghong in November 2018
c. Reduced investment by 12.6% from the original announcement by reducing capacity or 10 process units and eliminating 8 product units. However, refinery capacity remained unchanged, and PX capacity in fact increased from original 2.8 to 4.0 MMt/y. Ethylene capacity will also increase from 1.2 to 1.4 MMt/y.
d. A new project which is under environmental impact Assessment.
e. A new project in three phases in Shandong Province. The first phase with investment of $20bn has been approved and under environmental evaluation. The projects are focusing on petrochemical production. With each barrel of fuel production, 1.25 barrel of Teapot refinery capacity will be closed to reduce the refinery over capacity.

Figure 21 – PX focused Crude to Chemicals Capital Investments (S&P Global Commodity Insights, 2024)

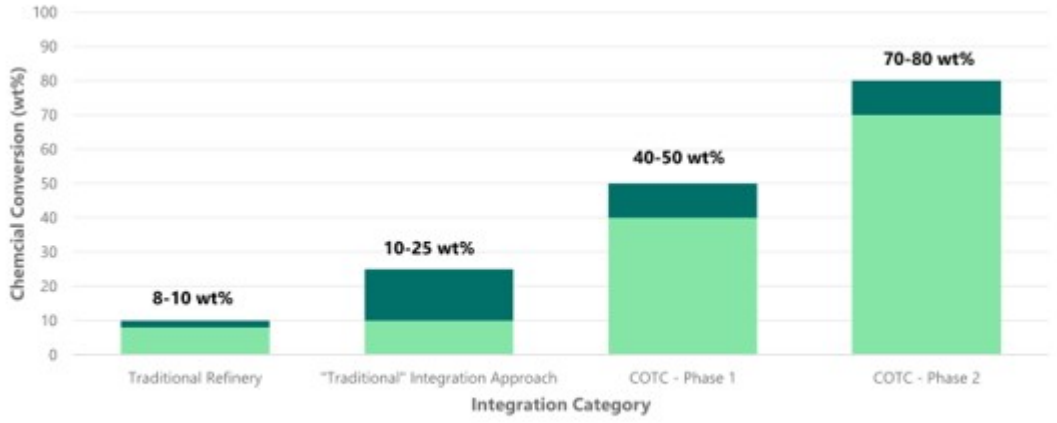

Figure 22 – Petrochemicals Yield Comparison (Wood Company, 2024)

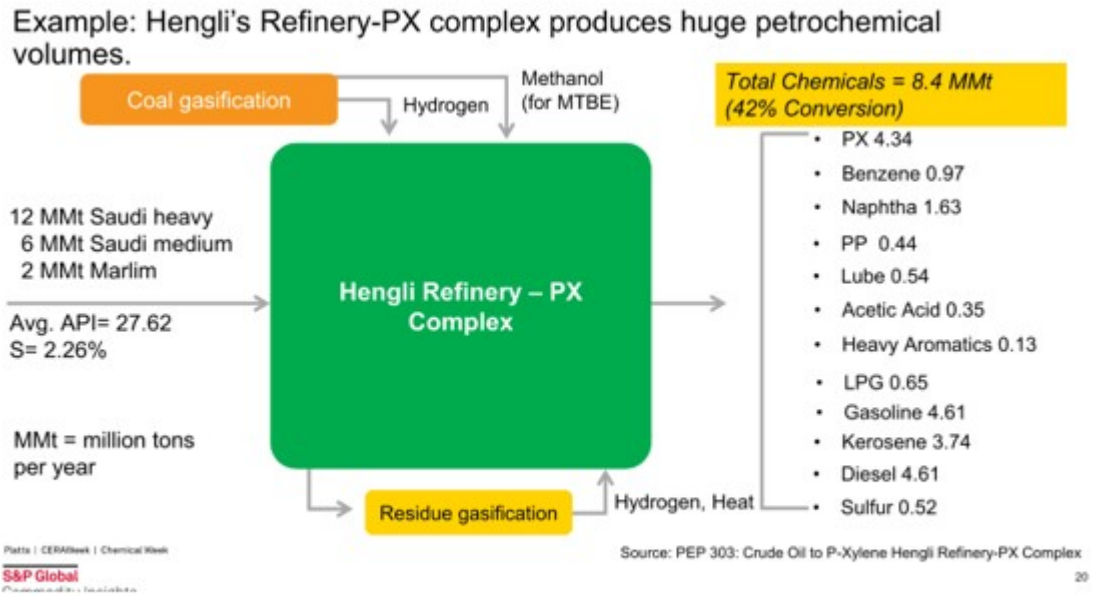

Figure 23 – Petrochemicals Yield for the Hengli Crude to Chemicals Complex (S&P Global Commodity Insights, 2024)

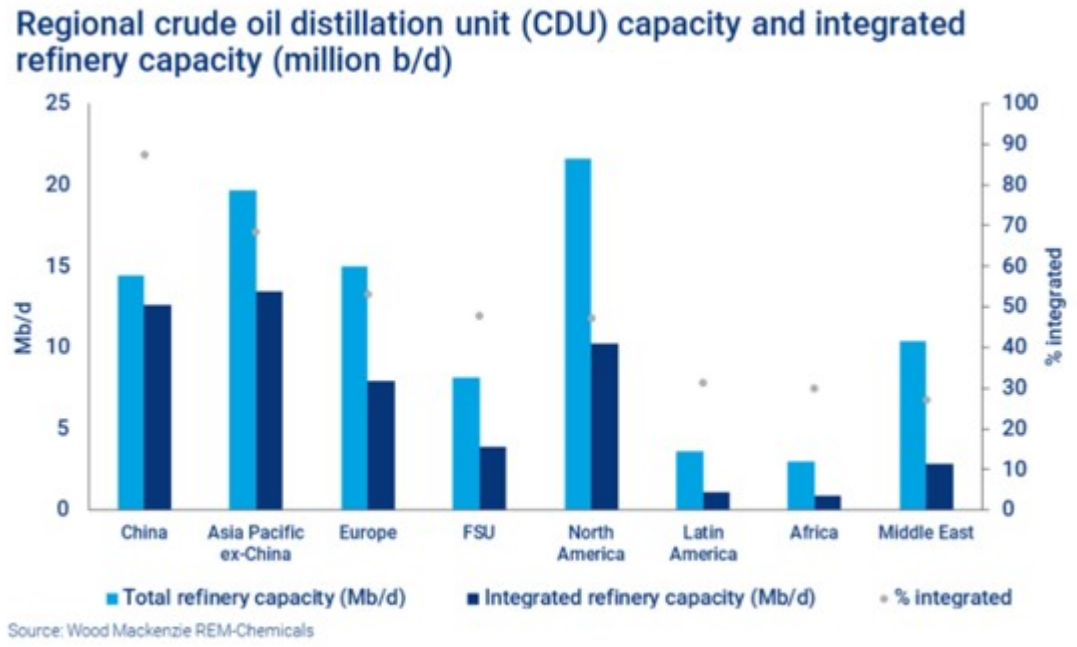

Figure 24 – Crude Oil Distillation Capacity and Integrated Refinery Capacity for Each Continent (Wood Mackenzie, 2023)

Figure 24 shows that the Asian players have a superior integration capacity of their refining assets in comparison with another continents, as mentioned above, this can be translated in a significant competitive advantage to the Asian players and a great potential o competitive imbalance of the downstream market considering the recent forecasts which indicates growing demand for petrochemicals. Furthermore, it's possible to see the power of the China in the Asian and global downstream market.

As aforementioned, face the current trend of reduction in transportation fuels demand at the global level, the capacity of maximum adding value to crude oil can be a competitive differential to refiners. Due to the high capital investment needed for the implementation that allows the conventional refinery to achieve the maximization of chemicals, capital efficiency becomes also an extremely important factor in the current competitive scenario as well as the operational flexibility related to the processed crude oil slate.

Recently, Lummus Company announced the implementation of your proprietary crude to chemicals technology, called TC2C™ (Thermal Crude to Chemicals) by a big player of the downstream industry in the Asian

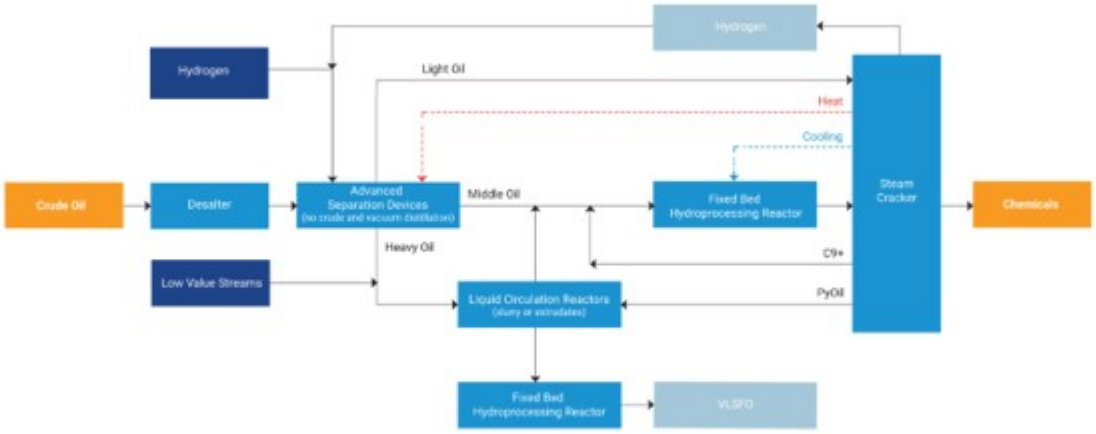

Figure 25 – Block Diagram for the TC2C™ Crude to Chemicals Technology by Lummus Company

market, reinforcing the growing trend of crude to chemicals in the Asian continent. The TC2C™ process can reach a yield of 70% in mass of high value petrochemicals from light crudes as informed by the licensor. Figure 25 presents a block diagram for this technology.

Available Crude to Chemicals Processing Routes

Nowadays, there are three technically available routes that are considered to capital investments to crude to chemicals refining complexes. Figure 26 presents the concepts based on the information of S&P Global Commodities Insights Company.

The conventional routes consider the processing of crude oil in a conventional crude oil refinery, producing petrochemical intermediates like naphtha which is supplied to a petrochemical asset like a steam cracking unit. The Henyi ExxonMobil route is based on the direct feed of selected crude oils, normally light and low contaminants crudes, to petrochemical assets, while the Chinese enterprise Hengli Zhejiang Shenghong project consider the feed of mixed crude oil slate to a crude to PX (Para-Xylene) complex to ensure the domestic Chinese market that present high demand by light aromatics (BTX). A conventional highly integrated refining hardware is capable to achieve 15 to 20 % of petrochemicals yield while a crude to chemicals refinery can reach up to 70 % as presented in Figure 22.

As aforementioned, the Aramco/Sabic concept is based on a high complexity refining hardware to convert selected crude oil (light) to maximize the yield of petrochemical intermediates, mainly light olefins.

Although the advantages presented by clos-

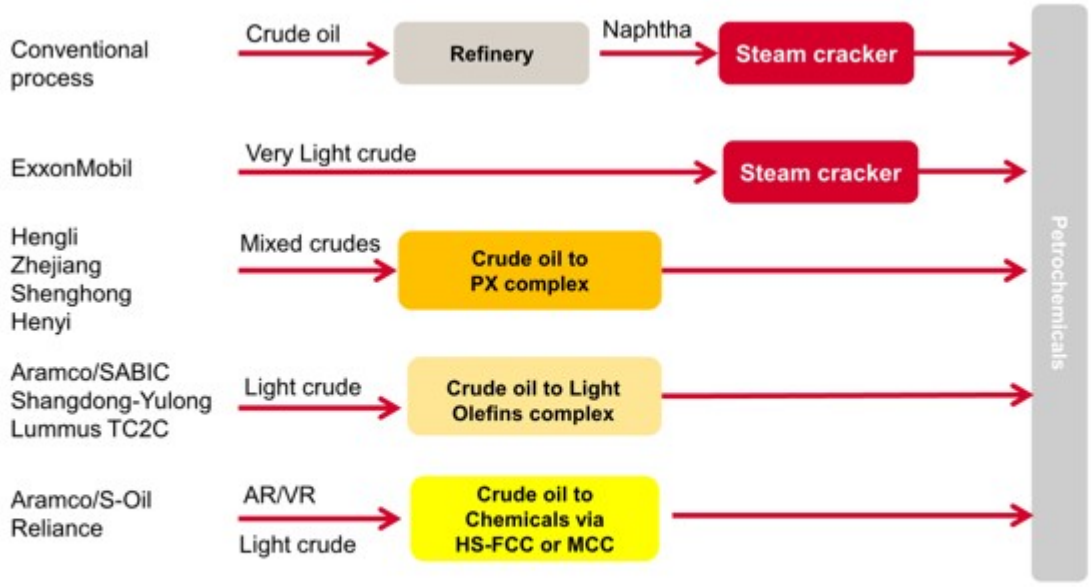

Figure 26 – Crude to Chemicals Concepts (S&P Global Commodities Insights Company, 2024)

petrochemical assets, it's important to understand that the players of downstream industry are facing a transitive period where, as presented in Figure 1, the transportation fuels are responsible for a great part of the revenues. In this business scenario, it's necessary to define a transition strategy where the economic sustainability achieved by the status (transportation fuels) needs to be invested to build the future (maximize petrochemicals). Keeping the eyes only in the future or only in the present can be a competitive mistake.

Conclusion

Nowadays, it is still difficult to imagine the global energetic matrix free of fossil transportation fuels, especially in developing economies. Despite this fact, recent forecasts, and growing demand by petrochemicals as well as the pressure to minimize the environmental impact produced by fossil fuels creates a positive scenario and acts as main driving force to closer integration between refining and petrochemical assets, in the extreme scenario the zero fuels refineries tend to grow in the middle term, especially in developed economies.

The synergy between refining and petrochemical processes raises the availability of raw material to petrochemical plants and makes the supply of energy to these processes more reliable at the same time ensures better refining margin to refiners due to the high added value of petrochemical intermediates when compared with transportation fuels. The development of crude to chemicals technologies reinforces the necessity of closer integration of refining and petrochemical assets by the brownfield refineries aiming to face the new market that tends to be focused on petrochemicals against transportation fuels, it's important to note the competitive advantage of the refiners from Middle East that have easy access to light crude oils which can be easily applied in crude to chemicals refineries.

Based on description above it's possible to apply the article published by W. Chan Kim and Renée Mauborge called "Blue Ocean Strategy" in Harvard Business Review, to classify the competitive markets in the downstream industry. In this article the authors define the conventional market as a red ocean where the players tend to compete in the existing market focusing on defeating competitors through the exploration of existing demand, leading to low differentiation and low profitability. The blue ocean is characterized by looking for space in non-explored (or few explored markets), creating and developing new demands and reaching differentiation. This model can be applied (with some specificities once is a commodity market) to the downstream industry, considering the traditional transportation fuels refineries and the petrochemical sector.

Due his characteristics, the transportation fuels market can be imagined like the red ocean, where the margins tend to be low and under high competition between the players with low differentiation capacity. On the other side the petrochemicals sector can be faced like the blue ocean where few players are able to meet the market in competitive conditions, higher refining margins, and significant differentiation in relation to refiners dedicated to transportation fuels market.

As presented above, the market forecasts indicate that the refiners able to maximize petrochemicals against transportation fuels can achieve highlighted economic performance in short term, in this sense, the crude oil to chemicals technologies can offer even more competitive advantage to the refiners with capacity of capital investment.

In the extreme side of the petrochemical integration trend, there are zero fuels refineries, as quoted above, it's still difficult to imagine the downstream market without transportation fuels, but it seems a serious trend and the players of the downstream sector need to consider the focus change in their strategic plans like opportunity and threat. As discussed above, even the players with less capital power can take actions to maximize the petrochemicals yield in their refining hardware. Despite this scenario, disruption is still a hard work in the case of downstream industry, but the crude to chemicals refining assets can produce a competitive imbalance in the market, especially due to the concentration of capital investments in the Asian market. The downstream industry has a history of adaptation of crude consumption patterns through the years and the crude to chemicals refining assets represents an evolution aiming to maximize the added value to the processed crude, reaching petrochemicals yield higher than 40 %.

The development of crude to chemicals technologies reinforces the necessity of closer integration of refining and petrochemical assets by the brownfield refineries aiming to face the new market that tends to be focused on petrochemicals against transportation fuels, it's important to note the competitive advantage of the refiners from Middle East that have easy access to light crude oils

which can be easily applied in crude to chemicals refineries. Recently one of the biggest petrochemical players, SABIC Company, announces the intention to make investments in a new crude to chemicals refinery with capacity of 400.000 barrels per day and the SATORP Company (A joint venture between Total Energies and Aramco companies) announced USS 11 billion dollars in capital investments in the Amiral petrochemical complex to promote closer integration with Jubail refinery (Saudi Arabia), reinforcing the trend of closer integration between refining and petrochemical assets in order to maximize the added value to the processed crude.

Less integrated refiners tend to compete in a kind of red ocean market where the refining margins tend to be lower due to the lower added value to the crude oil like transportation fuels, high sulfur fuel oil, and asphalt. Despite this, and according to the characteristics of the local markets, it's possible to achieve economic sustainability, in this case, capital discipline and operational efficiency are even more important for these players.

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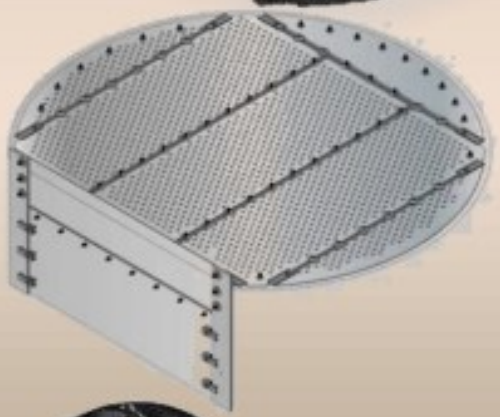

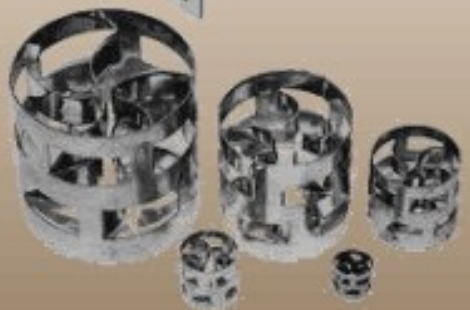

Atmospheric and Low Pressure Storage Tank Venting

Jayanthi Vijay Sarathy

Atmospheric storage tanks which store hydrocarbons are susceptible to vaporization and form explosive/flammable mixtures in the overhead regions of the storage tank. To attend to such a hazardous scenario, tank blanketing or nitrogen blanketing / padding methods are employed to prevent the flammable vapour content from coming into contact with air. Nitrogen is a popular choice to blanket the hydrocarbon vapours due to its inertness, low cost and availability.

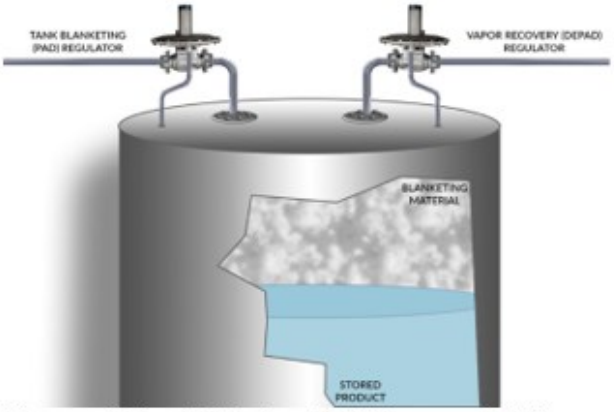

Figure 1. Tank Blanketing Schematic [1]

The nitrogen blanketing system consists of a inlet pressure regulator which receives the inert gas (e.g., nitrogen) to pressurize the tank based on a set point. When the pressure continues to rise, a second regulator, “de-pads” the tank by venting the blanketing gas (and acts as a back pressure regulator) to maintain the vapour pressure in the tank.

The following article explores how to size the tank blanketing system for atmospheric and low-pressure storage tanks, as per API 2000, 7th Edition, which is applicable to aboveground liquid petroleum or petroleum products storage tanks and aboveground and underground refrigerated storage tanks designed for operation at pressures from full vacuum through 103.4 kPag (15 psig).

General Notes

1. The basic sizing considerations for sizing the tank regulators and assigning its pressure settings, depends on tank inbreathing and outbreathing due to liquid movement and temperature changes. When a storage tank is getting filled, the vapour space in the upper deck experiences the pressure due to the rising liquid and the tank breathes out. During tank draining, there would be a fall in pressure which requires the tank to be able to breathe in and prevent it from imploding due to the vacuum created.
2. The key safety provisions in an atmospheric storage tank are an emergency relief valve, a Pressure vacuum relief valve (PVRV) and a blanketing line with regulator and sensing element. Each of these devices are operated based on a pressure set point, with the blanketing line acting as the first line of defence when the tank begins to experience overpressure. The PVRV acts as the second line of defence by breathing in or breathing out depending on the vapour pressure in the tank. The emergency relief valve kicks in when the tank pressure exceeds the design pressure. For flammable vapours in atmospheric storage tanks, these safety devices can also be fitted with a flame arrestor to prevent back propagation of any flame.
3. Apart from blanketing requirements due to liquid transfer and thermal effects, other possible causes of over pressurization must also be considered, as defined in Sec. 3.2.5 of API 2000, 7th Ed. Some examples being, if the hydrocarbon liquid is expected to flash because of high vapour pressure, the flashed-out vapour must be included when sizing the blanketing regulators. Volatile fluids are defined as tank products with a vapour pressure > 5 kPa.

4. To determine the venting requirements, the following conditions must be analysed as a minimum,
    - Normal Inbreathing due to max outflow of liquid from the tank
    - Normal inbreathing due to weather changes causing condensation of vapours
    - Normal Outbreathing due to maximum liquid inflow into the tank and max vaporization due to liquid transfer
    - Normal Outbreathing due to vaporization caused by thermal effects
    - Emergency venting due to fire exposure
5. As per section 3.3.1 of API 2000, 7th Ed, “When determining the venting requirements, the largest single contingency requirement or any reasonable and probable combination of contingencies shall be considered as the design basis. At a minimum, the combination of the liquid transfer effects and thermal effects for normal venting shall be considered when determining the total normal inbreathing or outbreathing”.
6. Additionally, except for refrigerated storage tanks, the common practice is to consider only total normal inbreathing for determining the venting requirements, because thermal inbreathing is a severe and short-lived condition.
7. As per API 2000, 7th Ed, the venting requirements are based on using hexane as a reference fluid since it gives results within an acceptable degree of accuracy for many fluids having similar fluid properties as that of hexane. The latent heat of vaporization of hexane is 334.9 kJ/kg with a molecular weight of 86.2 kg/kmol and assumes a vapour temperature of 15.60C for venting calculations.
8. Normal venting for pressure and vacuum can be accomplished using a PVRV with or without a flame arrestor. However, if open vents are used, a flame arrestor is a must when the stored liquid has a low flash point of < 60°C, or if the storage temperature can exceed the flash point. In case of heavy hydrocarbons like viscous oils or asphaltenes, where there is a risk of the flame arrestors getting plugged, open vents may be used as an exceptional case.
9. In case of emergency venting, the prescribed methods by API 2000, 7th Ed includes, larger open vents, larger PVRV, a gauge hatch that permits the cover to lift under abnormal internal pressure, a manhole that lifts when exposed to abnormal internal pressure, weak frangible roof to shell attachment, a rupture disc device or any other construction that aids in pressure relief.
10. Fixed roof tanks which have a weak (frangible) roof to shell attachment as described in API 650, the roof to shell connection will fail prior to other tank welds. Therefore, it is not necessary to consider emergency venting requirements. However, this does not mean the roof to shell connection can be allowed to fail, rather additional emergency vents can be provided to prevent the failure at the frangible point. For tanks which are < 15m in diameter, frangible roof to shell requirements is to be met.
11. When assigning the set pressures for the PVRV, it is often necessary to set (start to open) pressure be lower than the design pressure of the tank to allow for adequate flow capacity of the devices. The operating pressure must also be lower than the set pressure to allow normal pressure variations due to weather changes, or any other causes that affects the tank pressure.
12. For pressure relief scenarios, the calculated vapour flow will be at the actual pressure and temperature conditions of the vapour space in the tank. But this relief flow must be converted to an air-equivalent flow at normal or standard conditions. For vacuum relief scenarios, the calculated flow assumes ambient air inflow through the tank vent. If any medium other than air is used for vacuum relief, then it may be necessary to convert the flow rate to an air equivalent.
13. Tanks can be uninsulated, completely insulated, partially insulated or have a double walled arrangement to reduce vaporization. Typical values of Insulation for atmospheric storage tanks prescribed by API 2000, 7th Edition, is a heat transfer coefficient of 4 W/m2.K and a thermal conductivity of 0.05 W/m.K.

Case Study

A fixed roof storage tank of 15m dia and 20m max liquid level is blanketed using N2. The

liquid contents are assumed to be not volatile, and no flashing is expected. No flame arrestor is present. The design details are,

Assumptions

1. The location dependent temperature field of the tank wall and tank atmosphere are defined by their average temperatures.
2. The dependence of the heat transfer coefficient on the temperature difference is neglected.
3. The influence of the atmospheric pressure fluctuation is neglected. The vents start to function at a certain differential pressure.
4. No liquid residue is assumed to evaporate during any heating up.
5. The sun's radiation and ambient temperature is assumed to be constant

Methodology

The first step is to check if the fluid is volatile. Since the vapour pressure at the average storage temperature [2.5 kPa] is less than 5 kPa, the fluid is non-volatile, and no flashing occurs.

Venting Rates due to Liquid Transfer

The outbreathing rate due to liquid transfer expressed as m3/h of vapour at actual pressure and temperature conditions of tank vapour space as per Sec 3.3.2.2.1 of API 2000, 7th Ed is,

$$V_o = V_{pf} \quad (1)$$

Where,

V_{pf} = Max volumetric filling rate of non-volatile liquids [m^3/h]

$$V_o = 500\ m^3/h \quad (2)$$

Converting to Air-equivalent flow rate,

$$V_{o,Air} = \frac{V_o \times MW_{N_2}}{MW_{Air}} \times \sqrt{\frac{MW_{Air}}{T_{Norm\,[K]}}} \times \sqrt{\frac{T_{Storage\,[K]}}{MW_{N_2}}} \quad (3)$$

$$V_{o,Air} = \frac{500 \times 28}{29} \times \sqrt{\frac{29}{0+273.15}} \times \sqrt{\frac{20+273.15}{28}} \quad (4)$$

$$V_{o,Air} = 509\ m^3/h\ Air \quad (5)$$

Table 1. Design Details

Parameter	Value	Units
Latitude	32	degrees
Normal Pressure	101.325	kPa
Normal Temperature	0	^{0}C
MW of Air	29	kg/kmol
C_8 Vapour Pressure [20^{0}C]	2.5	kPa
Heat of Vapourization	334.9	kJ/kg
Relief Temperature	15.6	^{0}C
MW of Tank Fluid	86.2	kg/kmol
Avg. Storage Temperature	20	^{0}C
Liq. Vapour Pressure [20^{0}C]	2.5	kPa
Max Filling Rate	500	m^3/h
Max Drain Rate	700	m^3/h
MW of Blanketing Gas	28	kg/kmol
MW in Vapour Space	28	kg/kmol
Avg. T of Blanketing Gas	20	^{0}C
Tank Type	Vertical	-
Tank Diameter [D]	15	m
Tank Height [H] [HHLL]	20	m
Tank Volume [V]	3,534	m^3
Tank Insulation	Partially Insulated	
% Surface Area Insulated	5	%
Inside HTC [h]	4	W/m^2.K
Insulation Thickness [l]	4	in
Insulation Thermal K [λ]	0.05	W/m.K

In case the fluid is volatile, i.e., the vapour pressure is more than 5 kPa, then the out-breathing flow rate is to be taken as 2 x Vpf as per (b) of Sec 3.3.2.2.1 of API 2000, 7th Ed.

The Inbreathing rate due to liquid movement can be calculated as per Sec 3.3.2.2.2,

$$V_{ip} = V_{pe} \quad (6)$$

V_{pe} = Max discharge volumetric rate [m^3/h]

$$V_{ip} = 700\ m^3/h \quad (7)$$

Converting to Air-equivalent flow rate,

$$V_{o,Air} = \frac{700 \times 14}{29} \times \sqrt{\frac{29}{0+273.15}} \times \sqrt{\frac{20+273.15}{28}} \quad (8)$$

$$V_{ip,Air} = 713\ m^3/h\ Air \quad (9)$$

Venting Rates due to Thermal Effects

The outbreathing rate due to thermal effects [VOT] expressed in Nm3/h Air is,

$$V_{OT} = Y \times V_{tk}^{0.9} \times R_i \quad (10)$$

Where,

Y = Latitude Factor [-]

V_{tk} = Tank Volume [m^3]

R_i = Tank Reduction Factor [-]

If the tank is not insulated, R_i =1

If the tank is fully Insulated,

$$R_i = R_{in} = \frac{1}{1+\left[\frac{h \times l_{in}}{\lambda_{in}}\right]} \quad (11)$$

Where,

h = inside heat transfer coefficient [$W/m^2.K$]

l_{in} =Insulation Wall thickness [m]

λ_{in} = Thermal conductivity [W/m.K]

If the tank is partially insulated,

$$R_i = R_{inp} = \left[\frac{A_{inp}}{A_{TTS}} \times R_{in}\right] + \left[1 - \frac{A_{inp}}{A_{TTS}}\right] \quad (12)$$

Where,

A_{TTS} = Total shell & roof surface area [m^2]

A_{inp} = Insulated surface area of tank [m^2]

If the tank is double walled,

$$R_i = R_c = 0.25 + 0.75\left[\frac{A_c}{A}\right] \quad (13)$$

Where,

A = Total shell and roof surface area [m^2]

A_c = Tank surface area not inside of the containment area [m^2]

The latitude factor [Y] can be taken from Table 1 in Sec 3.3.2.3.2 of API 2000, 7th Ed as,

Table 2. Y Factor [Sec 3.3.2.3.2, API 2000, 7th Ed]

Latitude	Y Factor
Below 42^0	0.32
Between 42^0 and 58^0	0.25
Above 58^0	0.20

Therefore, applying the above expressions for a partially insulated tank,

For a latitude of 32^0, Y = 0.32

Volume of Tank [V_{tk}] = 3,534 m^3

$$R_i = \frac{1}{1+\left[\frac{4 \times 0.1}{0.05}\right]} = 0.1111 \quad (14)$$

$$R_i = R_{inp} = [0.05 \times 0.1111] + [1 - 0.05] \quad (15)$$

$$R_i = R_{inp} = 0.9556 \quad (16)$$

Therefore, the outbreathing rate due to thermal effects becomes,

$$V_{OT} = 0.32 \times 3534^{0.9} \times 0.9556 \quad (17)$$

$$V_{OT} = 477\ Nm^3/h\ Air \quad (18)$$

To estimate the thermal inbreathing rates, the condition is checked whether the tank contents are like hexane. Given that the liquid's vapour pressure of 2.5 kPa is like hexane at 20^0C, the inbreathing rate is computed as,

$$V_{IT} = C \times V_{tk}^{0.7} \times R_i \quad (19)$$

Where,

C = Factor depending on vapour pressure, latitude and average storage temperature [-]

V_{tk} = Tank Volume [m^3]

R_i = Tank Reduction Factor [-]

Table 3. Y Factor [Sec 3.3.2.3.3, API 2000, 7th Ed]

Latitude	C Factor			
	Vap Pressure like C_6		Vap Pressure > C_6 or unknown	
	Avg. Storage Temperature [^{0}C]			
	< 25^0C	≥ 25^0C	< 25^0C	≥ 25^0C
Below 42^0	4	6.5	6.5	6.5
Between 42^0 and 58^0	3	5	5	5
Above 58^0	2.5	4	4	4

Therefore, applying the corresponding values,

For a latitude of 32°, average storage temperature of 20°C, and a vapour pressure of 2.5 kPa like hexane at 20°C, C = 4.

Thermal inbreathing is therefore,

$$V_{IT} = 4 \times 3534^{0.7} \times 0.9556 \quad (20)$$

$$V_{IT} = 1{,}164\ Nm^3/h\ Air \quad (21)$$

Total Venting Rates

The total inbreathing and outbreathing rates are thus a sum of venting due to liquid transfer and thermal effects.

$$Total\ Inbreathing[V_{in}] = 1164 + 713 \quad (22)$$

$$V_{in} = 1{,}877\ Nm^3/h\ Air \quad (23)$$

$$Total\ Outbreathing[V_{in}] = 477 + 509 \quad (24)$$

$$V_{in} = 986\ Nm^3/h\ Air \quad (25)$$

Pressure Settings for Tank Blanketing

The pressure settings for the storage tank can be made based on the backpressure experienced in the flare header against the outbreathing PV regulator valve.

In the current undertaking, it is assumed the flare header ΔP until the outbreathing PV regulator is 2.0 kPa. The PV backpressure is taken to be 5 kPag.

The various pressure losses across the tank safety devices and pressure alarm settings are set as follows,

$$PV\ \Delta P = \left[\frac{1}{3}\right] \times Flare\ Header\ \Delta P \quad (26)$$

The PV ΔP [kPa] across the outbreathing PV regulator is taken to be at least 1/3rd of the pressure loss in the flare header line for good controllability. The remaining pressure settings in kPa and kPag are as follows,

$$PV\ Inlet\ P = PV\ \Delta P + PV\ backpressure \quad (27)$$

$$PV\ Crack\ Open\ P = PV\ Inlet\ P - 1 \quad (28)$$

$$High\ Pressure\ Alarm\ [PAH] = PV\ Inlet\ P + 1 \quad (29)$$

$$PVRV\ Set\ Point\ (SP) = PAH + 1 \quad (30)$$

$$PVRV\ (Out)\ Full\ Open = PVRV\ SP + 10\% \quad (31)$$

$$Bl\ Vlv\ Crack\ Open\ P = PV\ Crack\ Open\ P - 2 \quad (32)$$

$$Bl\ Vlv\ Full\ Open = Bl\ Vlv\ Crack\ Open\ P - 1.5 \quad (33)$$

$$Low\ P\ Alarm\ [PAL] = Bl\ Vlv\ Full\ Open\ P - 1 \quad (34)$$

$$PVRV\ (In)\ Set\ Pressure\ (SP) = PAL - 1 \quad (35)$$

$$PVRV\ (In)\ Full\ Open\ P = PVRV(In)\ SP \pm 10\% \quad (36)$$

Note:

When PVRV Inbreathing SP is positive, then use negative sign in eq. 36. Ensure PVRV Inbreathing Set Pressure > PVRV Inbreathing Full Open Pressure. The term 'Bl Vlv' in the above equation set refers to blanketing valve.

The storage tank's Max / Min design pressure (DP) and emergency vent set point (SP) can be assigned as,

$$Tank\ Max\ DP = PVRV\ (Out)\ Full\ Open + 0.5 \quad (37)$$

$$Tank\ Min\ DP = PVRV\ (In)\ Full\ Open \quad (38)$$

$$Emergency\ vent\ SP = Tank\ Max\ DP \quad (39)$$

Applying the above expressions,

$$PV\ \Delta P = \left[\frac{1}{3}\right] \times 2 = 0.67\ kPa \quad (40)$$

$$PV\ Inlet\ P = 0.67 + 5 = 5.67\ kPag \quad (41)$$

$$PV\ Crack\ Open\ P = 5.67 - 1 = 4.67\ kPag \quad (42)$$

$$PAH = 5.67 + 1 = 6.67\ kPag \quad (43)$$

$$PVRV\ SP = 6.67 + 1 = 7.67\ kPag \quad (44)$$

$$PVRV\ (Out)\ Full\ Open = 7.67 \times 1.1 = 8.43\ kPag \quad (45)$$

$$Bl\ Vlv\ Crack\ Open\ P = 4.67 - 2 = 2.67\ kPag \quad (46)$$

$$Bl\ Vlv\ Full\ Open = 2.67 - 1.5 = 1.17\ kPag \quad (47)$$

$$Low\ P\ Alarm\ [PAL] = 1.17 - 1 = 0.17\ kPag \quad (48)$$

$$PVRV\ (In)\ SP = 0.17 - 1 = -0.83\ kPag \quad (49)$$

$$PVRV\ (In)\ Full\ Open\ P = -0.83 + (-0.83 \times 0.1) \quad (50)$$

$$PVRV\ (In)\ Full\ Open\ P = -0.92\ kPag \quad (51)$$

$$Tank\ Max\ DP = 8.43 + 0.5 = 8.93\ kPag \quad (52)$$

$$Tank\ Min\ DP = -0.92\ kPag \quad (53)$$

$$Emergency\ vent\ SP = 8.93\ kPag \quad (54)$$

Emergency Venting

For the case of a tank not provided with a frangible / weak roof to shell attachment, the emergency flow capacity for fire relief can be estimated as,

$$q = 906.6 \times \frac{Q \times F}{L} \times \sqrt{\left[\frac{T}{MW}\right]} \quad (55)$$

Where,
q = Required flow capacity [Nm^3/h Air]

Q = Heat input from fire exposure [Watts]

F = Environmental factor [-]

MW = Molecular weight of vapour [kg/kmol]

T = Relieving vapour temperature [K]

L = Latent Heat of Vapourization of the stored liquid at the relieving pressure and temperature [J/kg]

It is assumed that the relieving vapour temperature corresponds to the bubble point of the stored liquid at relieving pressure. The heat input [Q] can be computed based on the wetted surface area and max design pressure of the storage tank from Table 3 of Sec 3.3.3.3.2 of API 2000, 7th Ed as follows,

Table 4. Q Value [Sec 3.3.3.3.2, API 2000, 7th Ed]

Wetted Surface Area[A_{TWS}]	Design Pressure	Heat Input [Q]
[m^2]	[kPag]	[W]
< 18.6	≤ 103.4	$63105 \times A_{TWS}$
≥ 18.6 and < 93	≤ 103.4	$224200 \times [A_{TWS}^{0.566}]$
≥ 93 and < 260	≤ 103.4	$630400 \times [A_{TWS}^{0.338}]$
≥ 260	> 7 and ≤ 103.4	$43200 \times [A_{TWS}^{0.82}]$
≥ 260	≤ 7	4,129,700

For vertical tanks, the wetted area is equal to the total surface area of the vertical shell to a height of 9.14 m above grade. For a vertical tank setting on the ground, the area of the ground plates is not included as wetted area. For a vertical tank supported above grade, it is necessary to include a portion of the area of the bottom as additional wetted surface. The portion of the bottom area exposed to a fire depends on the diameter and elevation of the tank above grade. It is necessary to use engineering judgment in evaluating the portion of the area exposed to fire.

In the current example, since the height of the tank is much greater than 9.14 m, the max height for emergency venting is taken to be 9.14 m. Therefore, the wetted surface area is,

$$A_{TWS} = \pi \times 15 \times 9.14 = 431\ m^2 \quad (56)$$

From Table 4, for a tank Max design pressure of 8.93 kPag and wetted surface area of 431 m^2, the heat input from fire exposure is,

$$Q = 43200 \times [431^{0.82}] = 6{,}244{,}783\ W \quad (57)$$

The F factor for an insulated tank with an insulation thickness of 4 inches as per Table 9 of 3.3.3.3.3 of API 2000, 7th Ed, is 0.075.

The relieving vapor temperature is 15.6°C and the latent heat of vaporization is 334,900 J/kg as per Sec 3.3.3.3.3 of API 2000, 7th Ed. Estimating the required flow capacity for emergency venting, we get,

$$q = 906.6 \times \frac{6{,}244{,}783 \times 0.075}{334{,}900} \times \sqrt{\left[\frac{15.6+273.15}{86.2}\right]} \quad (58)$$

$$q = 2{,}321\ Nm^3/h\ Air \quad (59)$$

Annexure F of API 2000, 7th Ed, provides guidance on what should be the blanketing (tank inbreathing) flow rates for flashback protection based on three levels of protection.

Level 1 offers minimum inert gas blanketing requirements with a specific flame arrestor classification. Level 2 offers more stringent blanketing requirements for different flame arrester classification. Level 3 provides the highest blanketing requirements with no flame arrestor.

As per Annex F, for the inert gas supply, minimum values of available inert gas volume [$\tilde{V}I$] and volume of reserve inert gas [Vi] are required. To determine the amount of reserve inert gas, the volume of the applicable parts in the piping up to the air separation unit should be considered.

The inert gas blanketing required flow rate [$\tilde{V}_I$] [m^3/h] and volume of reserve inert gas [V_i] [m^3] for the three levels is estimated as,

For Level 1

$$\tilde{V}_I[m^3/h] = [0.1 \times C \times R \times V_{tk}^{0.7}] + V_{pe} \quad (60)$$

$$V_i\ [m^3] = 0.04 \times V_{tk} \quad (61)$$

Where,

V_{pe} = Max rate of liquid discharge [m^3/h]

For Level 2,

$$\tilde{V}_I[m^3/h] = [0.2 \times C \times R \times V_{tk}^{0.7}] + V_{pe} \quad (62)$$

$$V_i\ [m^3] = 0.08 \times V_{tk} \quad (63)$$

For Level 3,

$$\tilde{V}_I[m^3/h] = [0.5 \times C \times R \times V_{tk}^{0.7}] + V_{pe} \quad (64)$$

$$V_i\ [m^3] = 0.12 \times V_{tk} \quad (65)$$

For

C = 4 ; R =0.9556,

V_{tk} = 3,534 m^3 ; V_{pe} = 700 m^3/h

Table 5. Blanketing for Flashback Protection

Parameter	Value	Units
Level 1 Inbreathing [$\tilde{V}_I$]	816	m^3/h
	831	Nm^3/h Air
Level 1 Vol of Res Inert gas	141	m^3
Level 2 Inbreathing [$\tilde{V}_I$]	933	m^3/h
	950	Nm^3/h Air
Level 2 Vol of Res Inert gas	283	m^3
Level 3 Inbreathing [$\tilde{V}_I$]	1,282	m^3/h
	1305	Nm^3/h Air
Level 3 Vol of Res Inert gas	424	m^3

Considering no flame arrestor is present, Level 3 inbreathing rates for flash protection of 1,282 m^3/h [1,305 Nm^3/h Air] is taken to size the PVRV.

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Appendix A

Site Conditions		
Latitude	32	degrees
Normal Pressure	101.325	kPa(a)
Normal Temperature	0	^{0}C
Molecular Weight [MW] of Air	29	kg/kmol
Vapour Pressure of Hexane at 20^{0}C	2.5	kPa
Heat of Vapourization	3,34,900	J/kg
Relief Temperature	15.6	^{0}C

Tank Liquid Properties		
Avg. Storage Temperature	20	^{0}C
MW of Tank Fluid	86.2	kg/kmol
Vapour Pressure of Liquid at 20^{0}C	2.5	kPa
Max Filling Rate	500	m^3/h
Max Drain Rate	700	m^3/h
MW of Blanketing Gas [Inbreathing]	28	kg/kmol
MW in Vapour Space [Outbreathing]	28	kg/kmol
Avg. Temperature of Blanketing Gas	20	^{0}C

Tank Details		
Tank Type	Vertical	-
Tank Diameter [D]	15.0	m
Tank Height [H] [HHLL]	20.0	m
Tank Liquid Volume [V]	3,534	m^3
Design Pressure [Emergency Vent SP	8.93	kPag

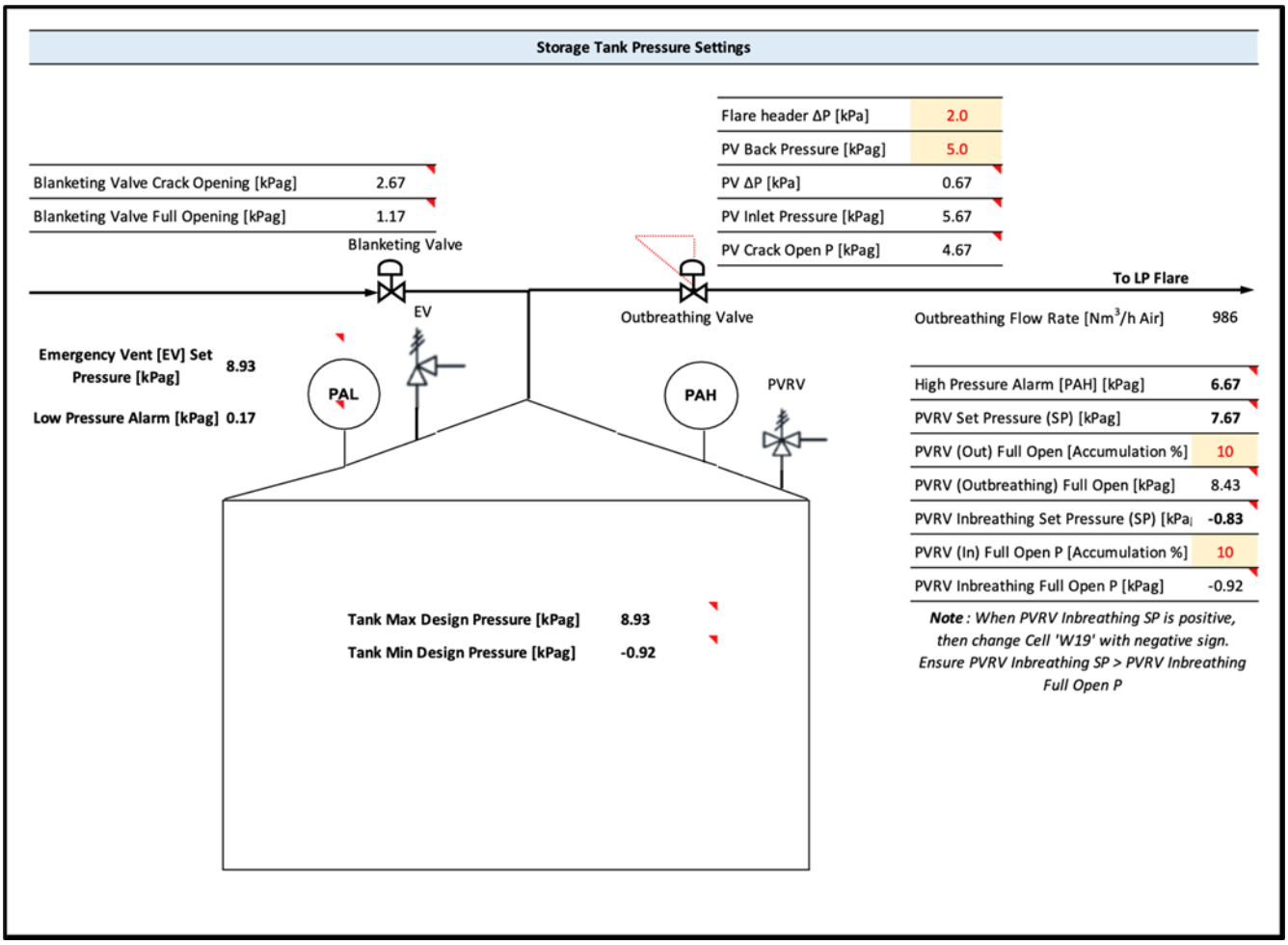
Liquid Movement [API 2000, 7th Ed]		
Is liquid Volatile / Non Volatile	Non Volatile	
Flashing during Filling	0	m^3/h
Liquid Movement Outbreathing Vol. Rate	500	m^3/h Bl. gas
	509	**Nm^3/h Air**
Liquid Movement Inbreathing Vol. Rate	700	m^3/h Bl. Gas
	713	**Nm^3/h Air**

Thermal Effects [API 2000, 7th Ed]		
Y Factor	0.32	-
Is the Tank Insulated	Partially Insulated	-
% Surface Area Insulated [A_{inp} /A_{TTS}] or [A_c/	5	%
Inside Heat Transfer Coefficient [h]	4	$W/m^2.K$
Insulation Thickness [l]	0.1016	m
Thermal conductivity of Insulation [λ]	0.05	W/m.K
Reduction Factor [R_i] [No Insulation]		-
Reduction Factor [R_{inp}] [Partial Insulation]	0.96	-
Reduction Factor [R_{in}] [Full Insulation]		-
Reduction Factor [R_c] [Double Walled Tank]		-
SUM of R	0.96	
Thermal Outbreathing Rate	**477**	**Nm^3/h Air**
Is Vapour Pressure Similar or < Hexane	Yes	-
C Factor	4	-
Thermal Inbreathing	**1,164**	**m^3/h Air**

Blanketing for Flashback Protection [Annex F, API 2000, 7th Ed]		
Level 1 Inbreathing [$\tilde{V}_i$]	816	m^3/h Bl. gas
	831	Nm^3/h Air
Level 1 volume of reserve inert gas	**141**	m^3
Level 2 Inbreathing [$\tilde{V}_i$]	**933**	m^3/h Bl. gas
	950	Nm^3/h Air
Level 2 volume of reserve inert gas	**283**	m^3
Level 3 Inbreathing [$\tilde{V}_i$]	**1,282**	m^3/h Bl. gas
	1,305	Nm^3/h Air
Level 3 volume of reserve inert gas	**424**	m^3

Emergency Venting [API 2000, 7th Ed]		
Wetted Height from Grade Level	9.14	m
Wetted Surface Area [A_{TWS}]	431	m^2
Heat Input from Fire Exposure [Q]	62,44,783	Watts
Tank Design	Insulated Tank	
Insulation Thickness [Only for Insulated Tan	4.00	inch
Environmental Factor [F]	0.075	-
Emergency Venting Capacity	**2,321**	**Nm^3/h Air**
Total Inbreathing	**1,877**	**Nm^3/h Air**
Total Outbreathing	**986**	**Nm^3/h Air**

Appendix B


Storage Tank Pressure Settings
Flare header ΔP [kPa] 2.0
PV Back Pressure [kPag] 5.0
PV ΔP [kPa] 0.67
PV Inlet Pressure [kPag] 5.67
PV Crack Open P [kPag] 4.67
Blanketing Valve Crack Opening [kPag] 2.67
Blanketing Valve Full Opening [kPag] 1.17
Blanketing Valve
To LP Flare
EV
Outbreathing Valve
Outbreathing Flow Rate [Nm3/h Air] 986
Emergency Vent [EV] Set Pressure [kPag] 8.93
Low Pressure Alarm [kPag] 0.17
PAL
PAH
PVRV
High Pressure Alarm [PAH] [kPag] 6.67
PVRV Set Pressure (SP) [kPag] 7.67
PVRV (Out) Full Open [Accumulation %] 10
PVRV (Outbreathing) Full Open [kPag] 8.43
PVRV Inbreathing Set Pressure (SP) [kPa -0.83
PVRV (In) Full Open P [Accumulation %] 10
PVRV Inbreathing Full Open P [kPag] -0.92
Note : When PVRV Inbreathing SP is positive, then change Cell 'W19' with negative sign. Ensure PVRV Inbreathing SP > PVRV Inbreathing Full Open P
Tank Max Design Pressure [kPag] 8.93
Tank Min Design Pressure [kPag] -0.92

How to... LIQUID DISTRIBUTORS All Basics to know about Liquid Distributors

Dr.-Ing. Volker Engel

Liquid distributors are essential and critical parts of all packed towers. Due to the large number of parameters (column diameter, phase ratio, number of drip points, operational range, ...), there are many different distributor types and designs.

This article covers the main types of liquid distributors, their operating principles, as well as the challenges and optimization options for their use.

Introduction

The most obvious task of a liquid distributor is to distribute liquid across the column cross-sectional area to wet the top layer of structured packings or the top of random packed beds.

The basic idea is to wet the cross-sectional area as evenly as possible. If the liquid is applied at specific drip points, this pattern should be uniform. Fig. 1 shows uniform patterns with different drip point densities for a-c. In the context of a perfect liquid distribution, representation Fig. 1d would be the ideal liquid distributor. Such a covering is achieved with spray distributors – however, such a distribution means that the gas flow passes through the liquid feed and inevitably entrains liquid droplets. This is why such spray distributors are mainly used for heat transfer (quench applications). For the liquid distribution at classical mass transfer applications, so-called gravity distributors are normally used.

Metering Elements

In gravity distributors, liquid is fed into open channels and pots and flows from there via openings onto the packing. These openings (called metering elements) can be at the bottom of the distributor, in its wall or in tubes.
The challenge in designing liquid distributors is not only to have a uniform distribution pattern, but also to have same conditions (same liquid level, no horizontal liquid velocity) at each drip point.

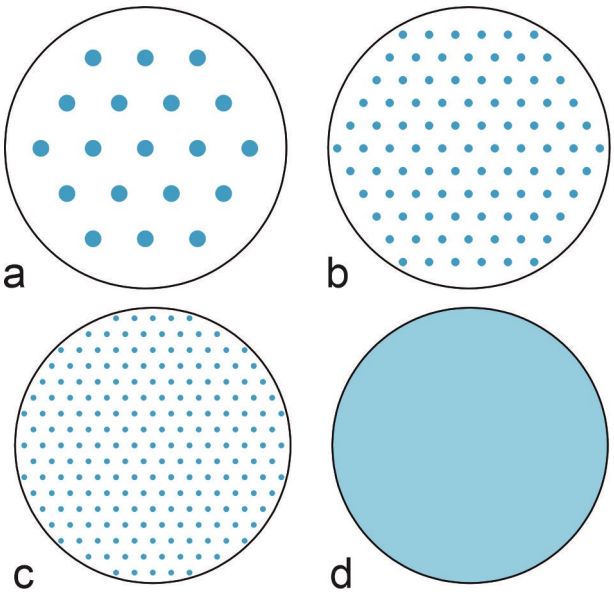


Fig. 1: Liquid distribution

BOTTOM HOLES

The liquid flow through a bottom opening (Fig. 2) depends on geometric and operational parameters. Shape, dimension and material thickness are defined by distributor design and are assumed to be constant (as long as there is no fouling or corrosion). The operational parameters lead to a liquid level h above the opening, a horizontal velocity within the liquid and a gas pressure drop Dp across the liquid distributor.

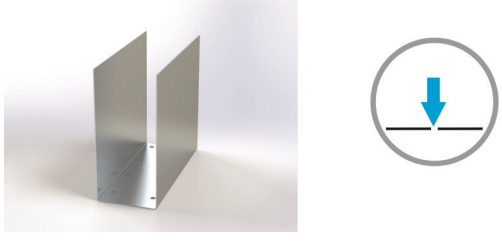


Fig. 2: Bottom holes

All these parameters are used to calculate the liquid volume flow rate through a single opening (eq. 1).

$$\dot{V}_{L,i} = \alpha \cdot A_{opening} \cdot \sqrt{2\left(g \cdot h - \frac{\Delta p}{\rho_L}\right)}$$

The orifice coefficient factor a is a function of the geometric parameters and also takes operational aspects into account.

For a certain a, the qualitative liquid flow rate through an opening can be plotted as shown in Fig. 3: On the y-axis, the liquid level above the opening is shown, the x-axis represents the liquid flow rate through the opening. This type of graph – calculated for an entire distributor – is called distributor characteristics.

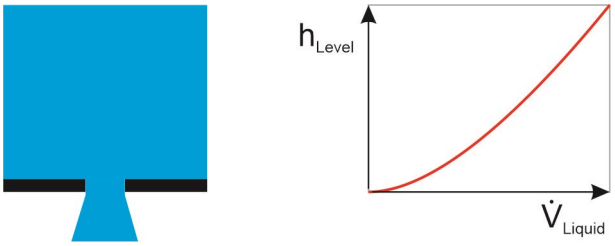


Fig. 3: Bottom hole characteristics

With the use of bottom holes, it is quite easy to design a uniform distribution pattern for the openings across the tower cross-sectional area. Additionally, it is easy to check the cleaning state of the openings at turnarounds. The main disadvantage of bottom holes is their blocking when (particle) fouling occurs. And at low liquid loads, the liquid might not detach from the bottom of the distributor and runs along the bottom side. By this, the liquid may accumulate at a certain drip point of the distributor. This effect may occur at low liquid flow rates, high liquid surface tension (e.g. aqueous systems) or high gas loads.

Lateral openings (Wall openings)

The liquid flow rate through a lateral opening (Fig. 4) is quite like that of a bottom hole. Equation eq. 1 is still valid, as long as the entire opening is filled by liquid. Of course, the orifice coefficient a is different from those of the bottom openings.

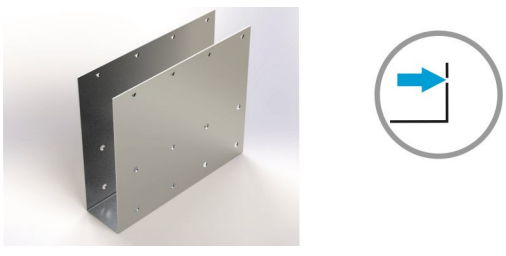


Fig. 4: Lateral holes

The qualitative liquid flow rate through a lateral opening in this case results as depicted in Fig. 5: The curve is like the bottom opening characteristics, but the opening only becomes active from a certain liquid level.

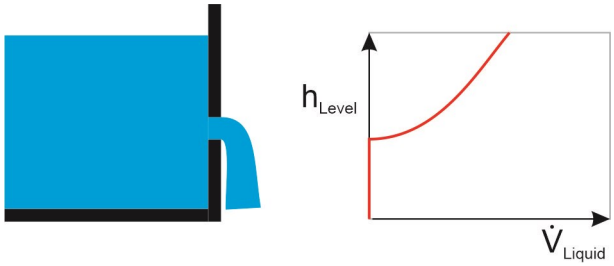


Fig. 5: Lateral hole characteristics

This type of opening withstands fouling, as long as the fouling hasn't filled the distributor up to this level. Additionally, it is possible to have openings at several levels in the wall. By this you can adapt a distributor for a high operation range (see later). But it is comparable difficult to clean (and check) those lateral openings – especially when it is covered by a guiding tube.

Liquid from the opening is exposed to the gas and – unlike the bottom openings – may not flow vertical towards the packing. At high

surface tension and low liquid load you may observe liquid running along the walls and keeping to the bottom of the distributor. For this reason, guiding tubes are often added to the openings, to guide the liquid down the wall to the packing (Fig. 6). Those guiding elements are welded to the distributors or consist of back and front plate (removeable for cleaning).

Fig. 6: Guiding tubes for lateral openings

Drip tubes

The third type of metering elements is the drip tube (see Fig. 7). It combines the feature of the bottom hole (to have a liquid feed point anywhere in the distributor area) with the feature of the wall opening (not operating at the ground level of the distributor and therefore not struggling with fouling). One difference to lateral openings is the limiting cross-sectional area of the tube: If the opening(s) for the liquid are larger than the tube area, the liquid flow is limited by the tube.

Fig. 7: Drip tubes

The calculation is like that for the wall openings (see Fig. 8). The orifice coefficient for the opening in the tube is slightly different from that of the wall.

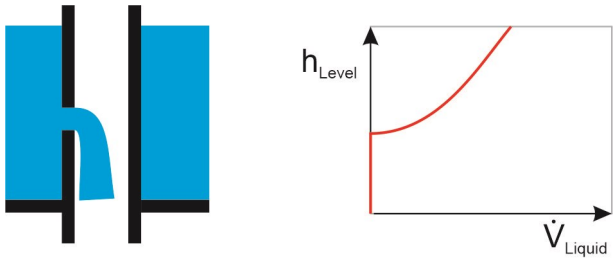


Fig. 8: Drip tube characteristics

Combination of metering elements

All three variants of metering elements are used in liquid distributors. To achieve a good liquid distributor quality at high liquid load ranges at acceptable installation height, the metering element types are combined.

Fig. 9 shows examples of those combinations.

This helps to reduce the height of the distributor for a certain load range. When there are certain load scenarios, you may link each load to a stage. Therefore, you will find distributors with three stages (one for MIN, one for DESIGN, one for MAX load).

The lower sketch in Fig. 9 demonstrates the combination of all metering element types. In practice you will not combine bottom holes with lateral openings: By combining bottom openings and lateral openings, the distribution pattern changes when the lateral openings get active.

Distributor types

In practice, three different types of gravity distributors are used: deck-type, pan-type and trough distributors. They vary in partitioning the column cross-sectional area to form a liquid volume from which the liquid drains onto the packing.

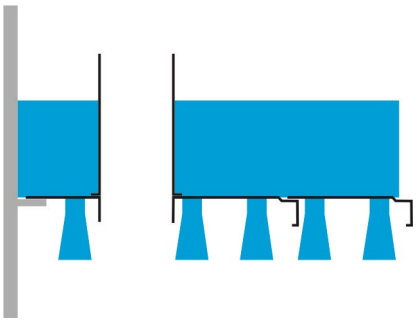
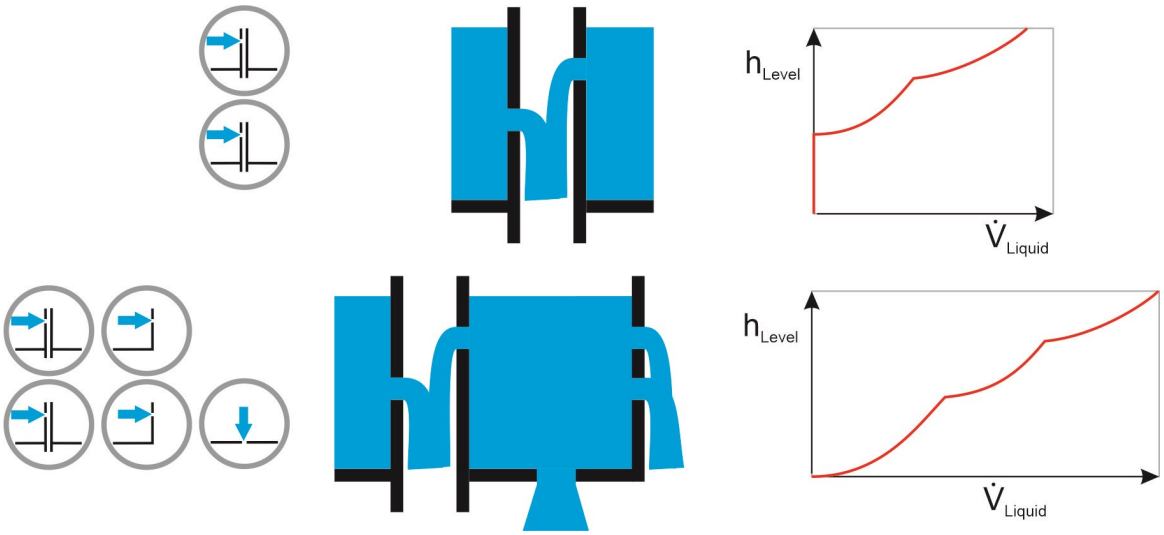


Fig. 10: Deck distributor

Deck distributor

A deck distributor is very similar to a chimney tray where the base panels are perforated and used for liquid distribution (Fig. 10). The panels are segmented with integrated beams as for standard trays. The risers are integrated into this base construction. For larger diameters, there are – of course – additional major beams. The distributor is placed (gasketed) on a full support ring.

By this, the desired equal distribution can be achieved by a good placement of the risers. Fig. 11 shows on the left the wanted distribution pattern, in the middle the placement of small risers without disturbing the pattern, and on the right larger risers (where some of the distribution points can't be realized; those lost elements are shown in red).



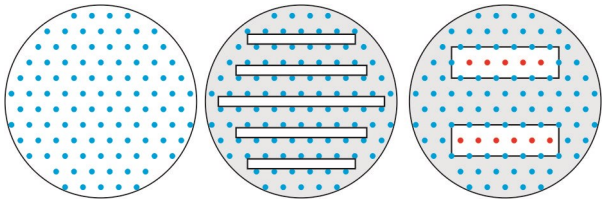


Fig. 11: Placement of risers at deck distributors

Metering elements used on a deck distributor are bottom holes and drip tubes as well as lateral openings in the gas risers.

The horizontal liquid velocity within the distributor volume should not be high (the value of 0.3 m/s is often considered as maximum). Any horizontal liquid velocity affects the orifice coefficient and leads to a hydraulic gradient resulting in different liquid levels within the distributor. Therefore, it is important to feed the distributor in a suitable way.

For high liquid loads and large diameters, the use of parting boxes (Fig. 12) helps to feed the right amount of liquid to the area where it will leave the distributor.

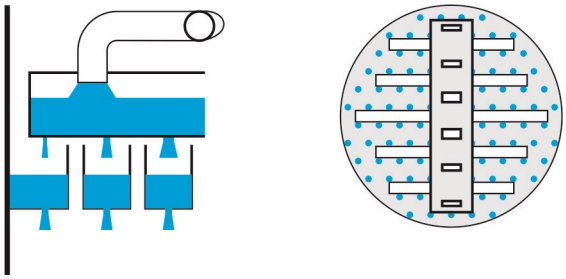


Fig. 12: Parting box for deck distributor

The advantages of deck distributors are good statics (robust) and it is easy to use them as re-distributors by adding roofs to the risers.

Deck distributors are not used for high quality distribution, because the panel segments interfere with the distribution pattern.

Pan-type distributor

Pan-type distributors are normally used for small column diameters.

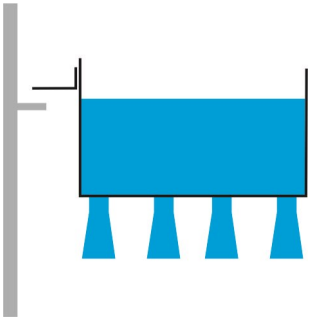


Fig. 13: Pan-type distributor

The distribution pattern of trough and deck-type distributor variants – typically used for large diameters – are normally equilateral, triangular or rectangular spaced. For pan-type distributors, you may find this type, too (Fig. 14a). But since the pan-type distributors are preferably used for small diameters, it is easier to have a radial-based pattern. It is point-symmetrical and therefore good for small dimensions (Fig. 14b).

To position a pan-type distributor on such a pattern, one can choose a certain diameter of the pan (Fig. 14c). The drip points in the outer area (the area for the gas flow) are lost and shown in red.

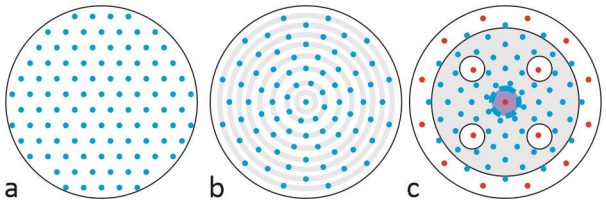


Fig. 14: Distribution pattern of pan-type distributors

Most of the pan-type distributors are working with bottom holes. Some of them are designed with drip tubes and lateral openings. At high gas load or at larger diameters, risers in the pan area are added. (If the entire gas flow is forced to pass the pan at the outer ring, there is the risk of generating a significant gas maldistri-bution. Since the void fraction at the tower shell of random packings is structurally higher, gas should not be led to this area.)

In small pans, the liquid is fed by a central pipe. For larger diameters and high liquid loadings, there will be an additional feed device (parting box).

Pan-type distributors are normally used for small tower diameters. In most cases, the pan is installed through the tower flange. (In rare cases you will find segmented pots for manhole installation.)

Trough Distributor

Trough distributors are the most flexible one and probably the distributor type which is used the most often.

The trough distributor consists of parallel troughs. The space between the troughs is the free area for the gas flow (Fig. 15).

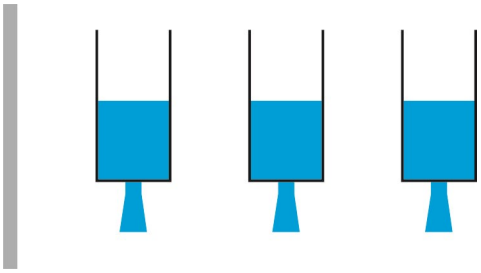


Fig. 15: Trough distributor

All metering elements discussed above can be used in trough distributors. The dimension of the troughs defines the appropriate metering element types. Fig. 16 shows the same distribution pattern for different trough widths (W). In Fig. 16a, troughs (width W) with ground openings are used, in Fig. 16b liquid is fed by wall openings (trough width 2W) and when the width of the troughs is 3W (Fig. 16c), there is the need of additional drip tubes in the center line of the trough.

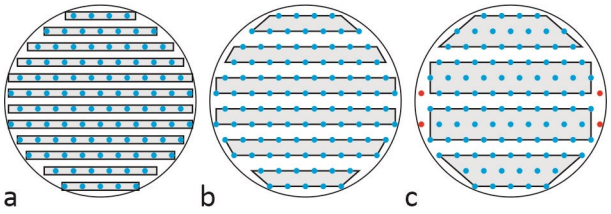


Fig. 16: Covering of distribution pattern by different sized troughs

Besides this variability for achieving a certain distribution quality (for different gas and liquid loadings), the advantages of this distributor type are good leveling and easy segmentation (for manhole passage).

As the distributor consists of many separate liquid volumes, it is very important to feed the correct amount of liquid to each of these compartments. Fig 17a shows the default of a parting box position: It is above the distributor troughs. Liquid flows through bottom or lateral openings from the parting box to distributor troughs.

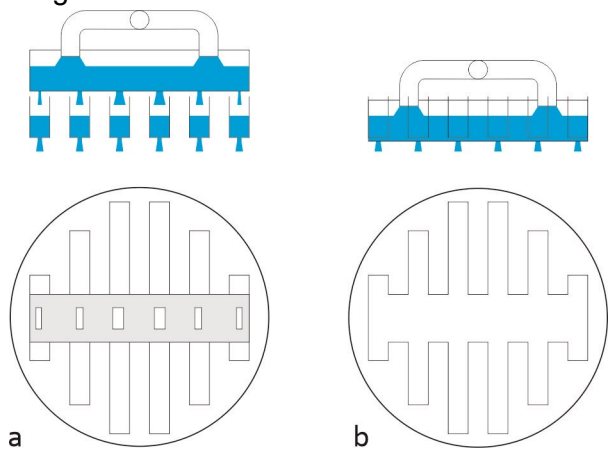


Fig. 17: Parting boxes for trough distributors (a: above troughs, b: inside troughs)

Because each distribution trough must receive exactly as much liquid as it releases, the openings in the parting box have to be adapted to the liquid flow rate for each trough! Precisely dosing by the parting box is very important!

Instead of positioning the parting box above the distribution troughs, you can integrate the parting box in the troughs (Fig 17b). This reduces the height of the distributor and all troughs are hydraulically connected by the parting box. As a result, any effect of different levels in the troughs is minimized, because liquid can equalize.

Feed to parting boxes

The parting box usually gets its fluid from a pipe or a pipe system (single pipe, T-Pipe, I-pipe with downpipes). To manage the transfer to the distribution troughs, the impulse of the liquid from the pipe system should be moderated. Fig. 18a shows a direct feed of a pipe to a trough. There are several designs for reducing the feed velocity. Those devices are called Calming devices. Fig. 18b-f show some calming elements to reduce the liquid impulse.

Flow multiplier / Dispenser

Fig. 19a shows a classical drip point, where liquid leaves the distributor and enters the packing at the vertical position. To enlarge the number of drip points – without changing

the number of metering elements – there are some special add-ons shown in Fig. 19b-d. They are called Flow multipliers, Dispensers, Fingers or Splitters. Fig. 19b shows a TNS distributor from KES. There is a square pot beneath the outlet and the liquid is spread to the packing by each corner. As a result, the original drip point is increased to 4 drip points.

Fig. 19c shows a design from KES-Montz. It is a pot with special fingers to guide the liquid, which split the liquid into 6 or 8 fingers equally.

Another idea of distributing drip points to a larger area is a so-called line distributor shown in Fig. 19d: The liquid from a hole is spread across a baffle plate and becomes a continuous liquid line. The next hole is positioned so that the liquid overlaps at the baffle.

Another (positive) effect of all these dispenser elements: The drip points are getting closer to the packing. This is a feature when there is a high gas flow rate, which can blow away falling droplets or streamlets and hinder them from entering the packing!

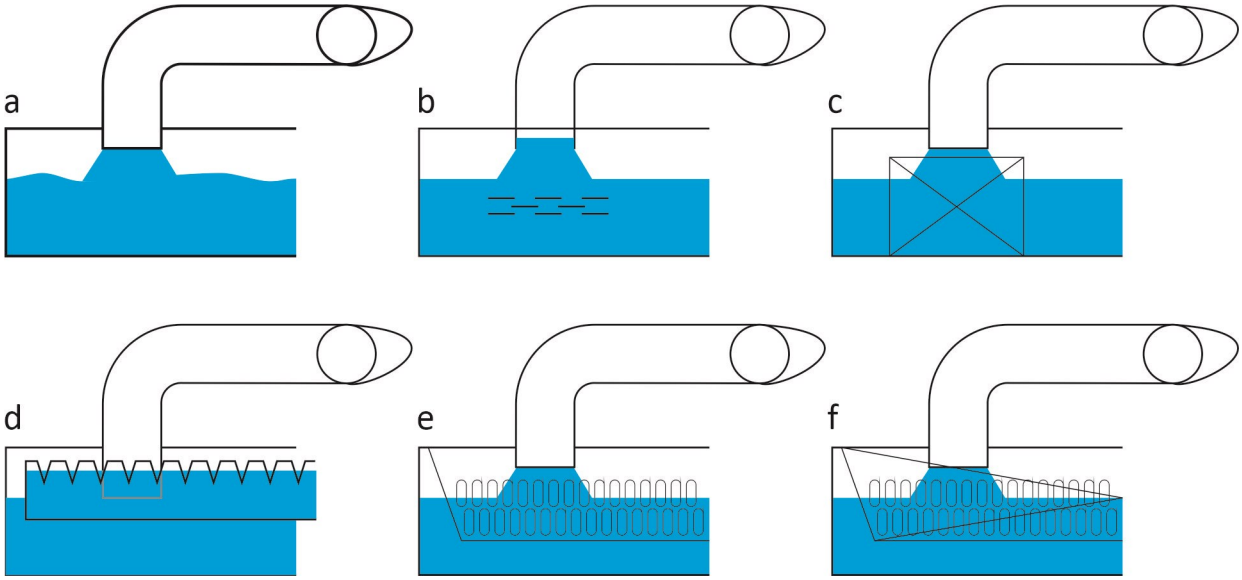


Fig. 18: Inlet of liquid to a parting box (a: direct input, b: staggered-slotted plates, c: packing block, d: weir trough, e: slotted box, f: slotted box filled with random packings)

Liquid distributor quality

As the above list of possible types and designs shows, there are very different distributors. In order to be able to compare their distribution efficiency and suitability, an objective statement on their distribution quality is desirable.

There are few contributions to this in literature. The best known is probably the publication by Moore/Rukovena [1] from 1987. It is an empiric approach to calculate a distribution quality value.

The basic idea of the model is to scale the area of the drip points according to the liquid flow. The area of all drip points equals the tower cross-sectional area. The liquid circle of each drip point is drawn. Out of this graph, three parameters are extracted: Fig. 20 shows the formation of these parameters for a simple distributor with 12 drip points.

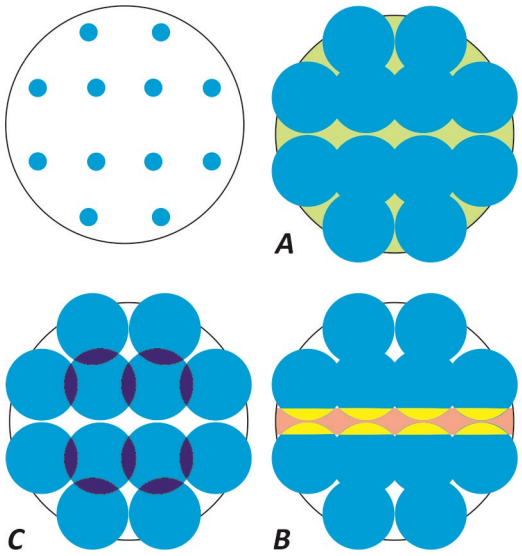


Fig. 20: Graphical determination of parameters A, B and C acc. to Moore/Rukovena

To cover most of the cross-sectional area, the liquid circles are partly outside the column and are overlapping. The remaining area

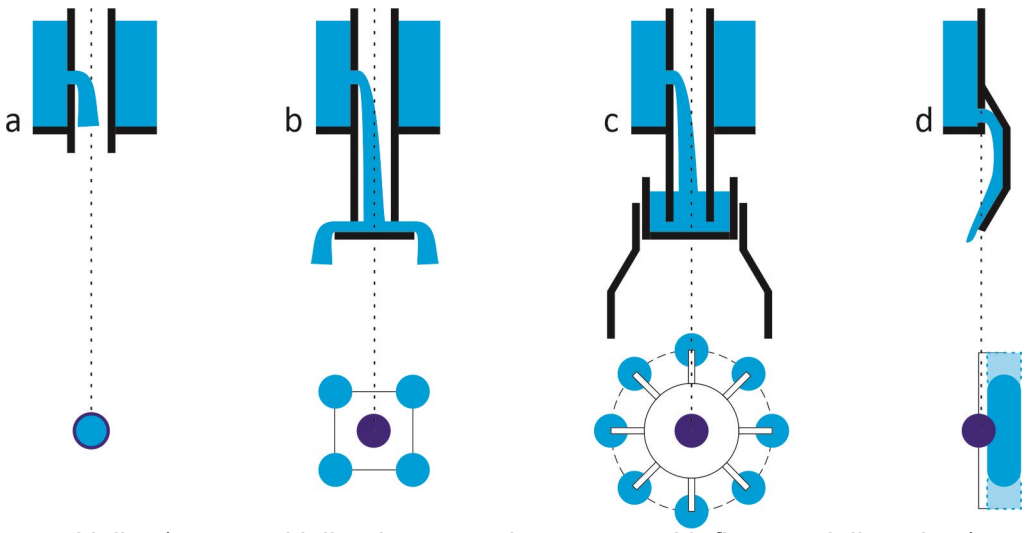


Fig. 19: Flow multiplier (a: no multiplier, b: square box. c: pot with fingers, d: line plate)

is shown in green (Fig. 20-A). The ratio of the blue covered area inside the column to the cross-sectional area is called parameter A in the model.

The overlapping area – shown in dark blue at Fig. 20-C – is named parameter C. In this example, the area is 'double irrigated'. But there may be three- or four-times irrigation at other layouts, too.

Parameter B defines the irrigation within one twelfth of the tower area where the highest or the poorest irrigation takes place. In the example shown, the center of the tower has a poor irrigation. The red area shows one twelfth of the tower. The liquid circles within this area are shown in yellow. Parameter B is the yellow area divided by the twelfth of the tower area.

$$Q = 0.4 \cdot (100\% - A) + 0.6 \cdot B - 0.33 \cdot (C - 7.5\%)$$

The distributor quality acc. to Moore/Rukovena is calculated by formula eq. 2.

Fig. 21 and Fig. 22 show some examples of common distributors evaluated by this quality calculation.

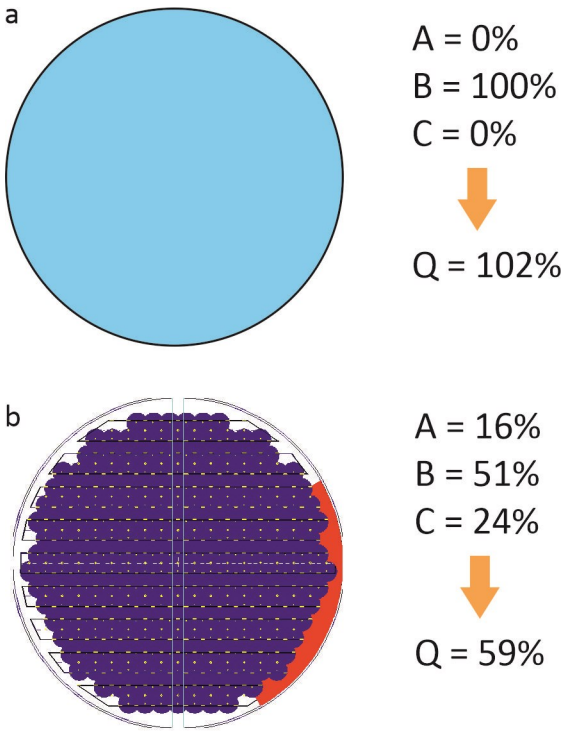


Fig. 21: Evaluation of distributor examples acc. to Moore/Rukovena

An ideal distributor is shown in Fig. 21a (Parameter A is 0%: all tower area is covered by liquid circles. Parameter B is therefore 100%: the twelfth of the tower area is ideally irrigated. Parameter C is 0%: No over-irrigation takes place).

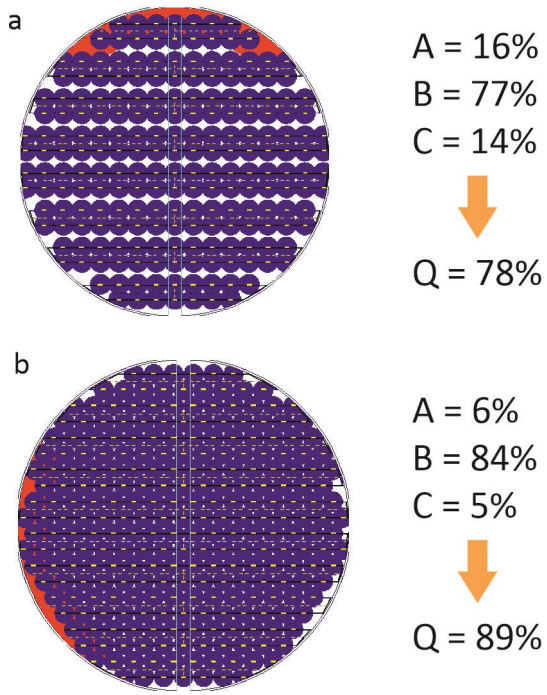


Fig. 22: Evaluation of distributor examples acc. to Moore/Rukovena

For a trough distributor with some distance to the tower shell (e.g. fastened at a support ring), the quality is about 59% (Fig. 21b).

Fig. 22a shows a standard TNT distributor (KES). Its quality value is about 78%. After optimizing the distribution pattern, you will gain a quality value of about 90% (Fig. 22b).

This empiric model is able to qualify a distributor in respect to its distribution pattern. It does not take into account, for which task the distributor is used.

Fig. 23 shows in principle the aspect of good and poor distribution quality in respect of the packing type: A perfect distribution is good for an open packing structure (high void fraction), where little maldistribution takes place. But note: At high gas load even a modern random packing as well as a structured packing will tend to squeeze the liquid to the wall.

A perfect distribution for a random packing of the first- or second-generation random packings (small void fraction) will lead to a high liquid wall ratio after considerable short bed length. The integral wetting of such a packing might be better by a poor liquid distribution (shown in Fig. 23 on the right). This illustrates the aspects of the discussion of distribution quality values.

The software TrayHeart [3] calculates the distribution quality of a liquid distributor for a certain packing type. The WELCHEM Cell model [2] is used to calculate the wetting of each

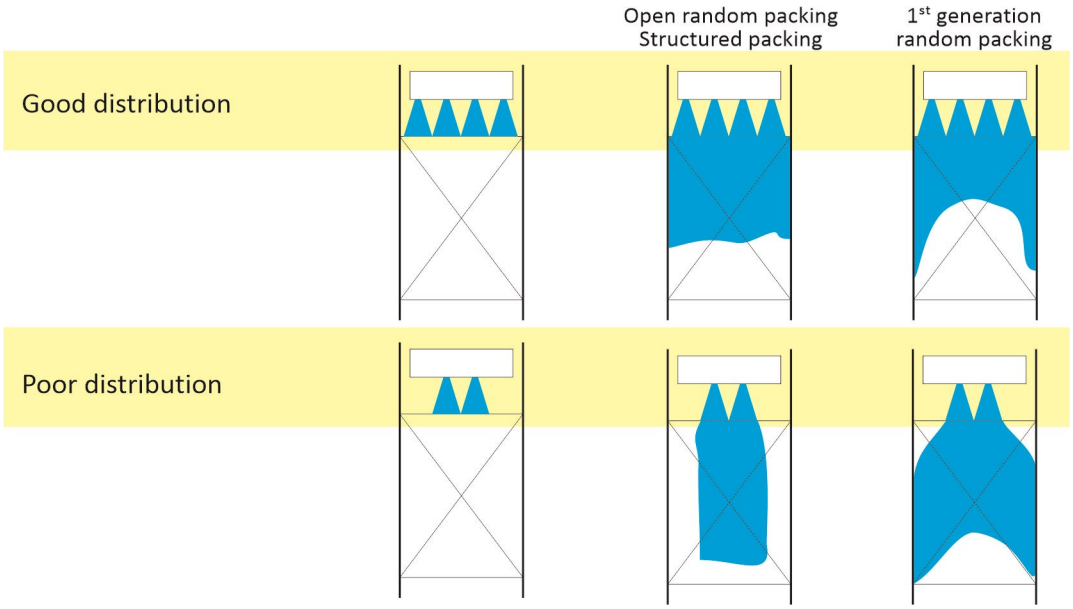


Fig. 23: Resulting flow in a packing

packing element and the distribution quality in each layer of the bed.

In this model, the dimension of the hexagonal cells is based on the size of the random packing elements. A perfect distribution would show the same liquid holdup of each cell (cells shown in green on Fig. 24). Any deviation lowers the distribution quality: Cells with high liquid holdup are shown in red, low holdup is shown in blue.

On Fig. 24 the distribution quality for a trough distributor above a random packing (1" Pall rings) is shown.

This can be used to evaluate the suitability of a distributor and the integral distribution quality of the bed, which indicates the need for redistribution.

At the top layer of the packing, the drip points of the distributor over-irrigates the corresponding cells. Liquid will spread to neighbor cells by trickling through the bed. The graph shows the cross-sectional distribution quality plots after 1m, 2m, 3m and 4m.

The blue curve shows the distribution quality per layer. The red curve is the liquid fraction at the column wall.

The mean distribution quality for the entire bed can qualify the distributor‘s quality for this type and length of packing.

With the same calculation method one can evaluate the need (and its potential benefit) of redistributing liquid after a certain bed length.

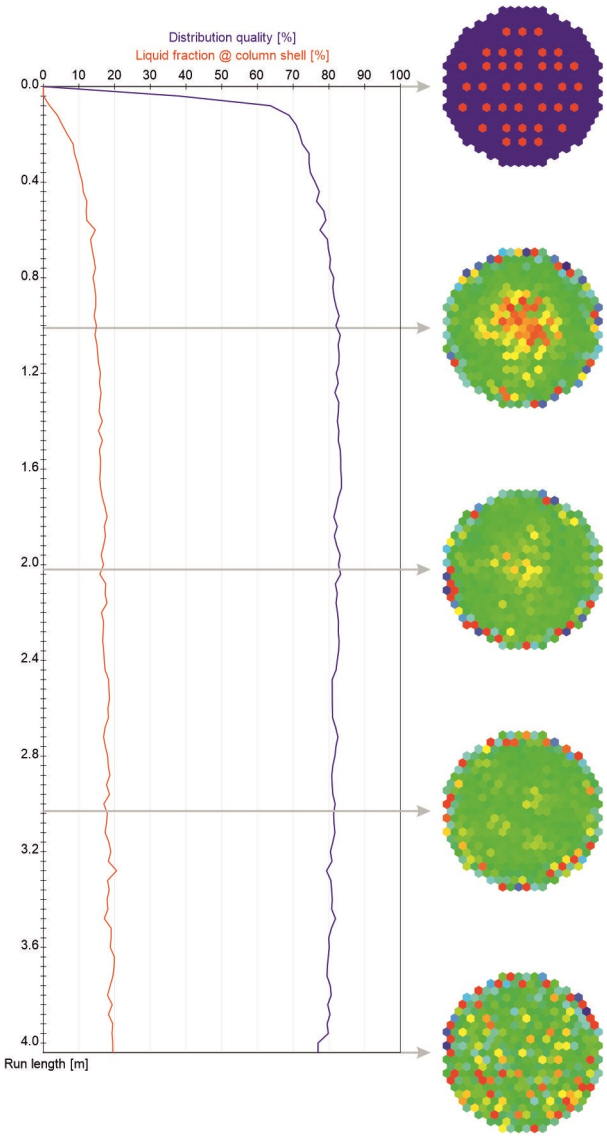


Fig. 24: Evaluation of distribution quality by WELCHEM Cell model [3]

Conclusion

Liquid distributors are vital components of packed towers, ensuring uniform liquid distribution over the column's cross-sectional area to optimize mass and heat transfer. There are three main types of metering elements: bottom holes, lateral openings, and drip tubes, each with unique advantages and limitations. Distributors can be categorized as deck, pan, or trough types, that are chosen based on tower dimensions and operational requirements. Proper distributor design and optimization enhance column performance while addressing challenges like fouling, gas-liquid interactions, and liquid maldistribution.

Author

Volker Engel studied process engineering at the Technical University of Munich and did his Ph.D. thesis on packed columns with Prof. Johann G. Stichlmair. Since 1998 he has been the managing director of WelChem Process Technology GmbH and head of the TrayHeart software. TrayHeart has developed into the state-of-the-art design tool for trays and internals in process technology.

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The View from Rock Bottom: Transforming Algae into a 'Biofactories' for Green Fuel Chemicals and Plastics… Current Efforts by Algenie, Et. Al.

Ron Cormier

Chlamydomonas pacifica algae growing in an outdoor pond
João Vitor Dutra Molino

Hello again to all, our most valued readership. Here in North and Central America, the seasons are turning, bringing drier weather, and colder temperatures. We hope this read for November finds you healthy, happy and in anticipation of the end-of-2024 holiday season. Every day, as we have for most of the 20th Century until now, our STEM expertise, skill, and care are applied to better sustain and manage traditional hydrocarbons value chains. As such, it seems timely to explore frustrating (but positive) current research and study into alternative means for these feedstocks, a strain of green algae that has been artificially evolved to turn carbon dioxide into sustainable fuel and plastic. By coupling Artificial Intelligence (AI), new control management can optimize production yields. Take a read and hopefully you all find these breakthroughs timely, interesting and engaging.

A newly discovered species of algae has been transformed through selective breeding and genetic engineering to survive and produce fuel in environments that would kill most organisms. The research is a step towards using algae-based “biofactories” to make sustainable alternatives to fossil fuels.

The new species, Chlamydomonas pacifica, was found in 2020 in a pond at the University of California in San Diego. The engineered strain can produce oil even when grown in wastewater at temperatures above 40°C (104°F), at a pH higher than 11, in full sunlight and in saline conditions – half as salty as the ocean.

Stephen Mayfield at the UC San Diego campus and his colleagues initially set out to find a species that thrives in highly alkaline

conditions and develop it for biodiesel production. In alkaline conditions, predators of the algae can't grow, and the water can hold more carbon dioxide. "The more CO2 you put in the water, that's food for algae and the faster they grow," says Mayfield.

With C. pacifica, the researchers not only discovered a highly alkaline-tolerant species, but one that can reproduce sexually. This meant they could use selective breeding to produce a strain with exceptional tolerance of high salinity, high light levels and high temperatures.

"There is no other extremophile algae that we know of that you can do breeding [with]," says Mayfield.

Like other green algae, C. pacifica produces fat to store energy as part of its normal life cycle. However, organisms that live in very harsh environments don't usually make good yields of commercially useful products, says Mayfield. "Most of the time, if an algae is growing under extreme conditions, their main job is just to stay alive."

To make C. pacifica more useful, the researchers inserted genes from soya beans that are known to increase fat production in other algae species. The result was an increase in fat content from 28 per cent in the parent strain up to 36 per cent in the engineered version.

In a separate process, the fats can be converted into biodiesel or polyurethane, a kind of plastic used in waterproof fabrics and many other applications. Mayfield says shoes made from algae-based materials are already approaching a similar cost to those made from petroleum-derived substances and have the benefit of being fully biodegradable when disposed of.

Similar to Mother Nature, But Faster….

Turning to algae to create oil makes sense. Many of the natural resources we use today came from extremophile bacteria and algae in the deep past, says Mayfield. "That is where 100 per cent of our petroleum comes from," he says. "That's why we have these enormous fossil fuel reserves, because for hundreds of millions of years extremophile algae turned an atmosphere that was 20 per cent CO2 and very low oxygen into an atmosphere that is 20 per cent oxygen today, with CO2 only a fraction of a percent. And where did all that CO2 go? It went into what we know as fossil fuels, ancient algae oil."

Sidney Australia startup Algenie, has come out of stealth with early funding for its photo-bioreactors that can create sustainable fuels, plastics and feed from algae. Armed with helix-shaped photo-bioreactors that can dramatically reduce the cost of production, Algenie is innovating with algae to replace planet-harming fossil fuels.

Emerging from stealth today, it has obtained A$1.1M ($730,000USD) in early funding from Better Bite Ventures, the University of Technology Sydney (UTS), and other investors, aiming to use the capital to build on its initial work of creating "carbon-positive" plastics and biofuels with algae through its next-gen bioreactors.

"Our helix design and technology is a true breakthrough, paving the way for algae-based solutions to become economically competitive with and ultimately replace traditional fossil-fuel-based products," says founder and CEO Nick Hazell (who previously founded plant-based meat company v2food).

The financing will help Algenie "obtain the clear evidence points" it needs to demonstrate its breakthroughs. "This relates to both the bioreactor performance and construction itself, as well as the biotech tools we are developing with UTS to create the optimal strains of algae and cyanobacteria," he tells Green Queen.

"We're not limited to just plastics," reveals Hazell. "Algae can be used to create everything from food and feed to biofuels and even building materials. The versatility of algae is a result of our ability to engineer different strains to produce specific chemicals and compounds, similar to how yeast is used in various industries." The incredible new tech that can recycle all plastics, forever.

Wider interest in the tweaked C. pacifica is taking off. A company in Australia has already asked for the strain to be sent for commercial evaluation. Labs around the world are now making elite strains of algae with similar potential to the new Californian one, says Peter Ralph from the University of Technology in Sydney.

In San Diego, for Mayfield's strain the big test is whether it can be successfully scaled up and survive in a large pond instead of in a container, says Ralph. He also says there is little risk of the engineered algae becoming a weed, since it only thrives under specific

extreme conditions. “As soon as it lands in a pond that has a pH of 7 and is 20°C [68°F], it won’t be competitive,” he says.

Mayfield suggests that algae like C. pacifica could one day survive on Mars and transform its environment. “There can be an extremophile algae that can terraform Mars just like there was an extremophile algae that terraformed Earth,” he says.

Algenie is looking to establish strategic partnerships with clients and is targeting a “more substantial fundraising round” in the coming months, according to Hazell.

How Algenie’s game-changing bioreactor works

While the sustainability potential of algae is well-known – it absorbs carbon to grow rapidly and captures more of the gas than any other ingredient or material. Some companies have been making plant proteins from seaweed, others have come out with DHA and EPA supplements, and a few are developing bio-based resins.

Algal cooking oil is also on the market now. But this industry has also witnessed a swathe of closures – from vegan seafood producer New Wave Foods and alt-milk maker Update Foods to biofuel company GreenFuel Technologies – a withdrawal of R&D funding and shifts away from businesses’ initial focus. This is because, largely speaking, this micro-plant has been too expensive to produce and difficult to scale up with conventional technology. So how does Algenie manage to overcome this hurdle?

The secret is in the bioreactor system. “The Algenie helical photo-bioreactor is based around thin-layer algae production, which maximizes growth per liter per day,” says Hazell. “LEDs and sophisticated light management ensure that every microalga gets the photons it needs when it needs them for optimal growth. We also optimise CO2, nutrition, and other variables to maximize the output to levels that are orders of magnitude more than existing systems,” he adds.

Algenie innovates with microalgae and cyanobacteria strains in collaboration with UTS, which works with algae from various collections, including CSIRO’s collection in Tasmania. “We select and optimize each strain according to the product we want to make for the customer we are partnering with. UTS biotech tools enable fast strain selection and optimization for hundreds of potential applications,” Hazell explains.

Once it identifies a product with a customer, Algenie digs into its database of strains that can deliver the required chemistry and selects a mutant with high levels of the desired output. “These elite strains are then optimized for high productivity using multiple parallel experiments orchestrated by an AI algorithm,” he says.

“Depending on the use case, the algae will be harvested by the customer and converted into the products that are needed. Our focus is on the lowest-cost biomass and chemistry production, but we will integrate our system into the customer’s downstream processing as needed. Of course, this will be different for a biofuel, plastic, a protein, or a pigment.”

Enabling highly efficient algae production and low costs

Algenie’s patented bioreactor design allows some algae species to double every two to three hours under ideal conditions. This is enough to produce 100 tons per year in the size of a shipping container – the equivalent of manufacturing 2.5 million soft drink bottles. At 10,000 tons per year in a hectare-sized field, the startup claims this yield is 3,000 times more efficient than conventional soy or corn crops.

“We use sophisticated sensors and algorithms to optimize the growth of the algae, which is continuously harvested and allows for a 24/7 production system that, in principle, need never stop. Algae systems have run for more than a year continuously, and this is one of the secrets behind our low-cost model,” says Hazell. Roughly 70cm in width, the helix winds can produce a ton of algae annually per unit. The design has the potential to bring production costs down by a factor of ten, totaling just $1 per kg of algae.

“Our ability to keep costs so low is a result of a combination of innovative design, efficient manufacturing, and strategic partnerships. Our unique helical photo-bioreactor design maximizes productivity per square meter, while our low-cost manufacturing process can deliver high-output bioreactors at a fraction of current capital costs,” explains Hazell.

“Additionally, our advanced AI and automation systems ensure optimal growth conditions, minimizing waste and maximizing

efficiency. These factors allow us to produce algae biomass at a cost that is competitive with traditional fossil fuels, making algae-derived products a more economically viable option.

“With capital costs lowered considerably, the cost of biomass becomes a function of the cost of renewable energy, which is falling rapidly, especially if we work together with major energy suppliers.”

More work needed to match fossil fuel polymers

Despite the many botched attempts, the algae biofuel market is expected to surpass $15B in value by the end of the decade. The global appetite for bioplastics, meanwhile, could cross $35B by that time. The algae market may be a fraction of the two above, but all these trajectories show that Algenie is in a space that isn’t going anywhere.

Simon Newstead, founding partner at Better Bite Ventures, feels Algenie has “the potential to reinvent algae production” while sequestering carbon at gigaton scales: “We got to know Nick through the APAC food tech ecosystem and believe his visionary leadership and deep technical expertise are perfect for this grand challenge.”

Fossil fuels are the main cause of greenhouse gas emissions, and plastics made from them are responsible for 3.4% of global emissions, a contribution higher than the entire aviation industry.
While Algenie hasn’t conducted a life-cycle assessment yet, preliminary work suggests that the dominant factor in emissions would be the conversion of carbon dioxide to biomass. This is “in the range of 2kg of CO2 to 1kg biomass, i.e., carbon-positive”, says Hazell. “The carbon footprint of the bioreactors themselves will be minor compared to the carbon-positive output of the algae produced,” he adds.

Plastic may take up to 500 years to decompose, but it’s popular because it’s useful. How does Algenie’s alternative compare in terms of durability and quality? “While there has been research into PHA and other bioplastics spanning many decades, there is more to be done to match every application currently met by fossil-fuel-derived polymers,” says Hazell.

“But if the cost structure and environmental impact are favorable, we believe that the industry will be incentivized to drive this. Biofuel research is also quite advanced through decades of research elsewhere, and the problem we are solving is cost and scalability,” he adds. With applications spanning not just fuels and plastics, but also textiles and fish feed, Algenie is also planning to licence its technology and collaborate with partners to co-invest in large-scale production infrastructure.

Wow! Interesting, isn’t it? We at Engineering Practice Magazine applaud these innovators both for next-tech means of improving our human way of life, but in an energy-saving and emissions-reducing conversion process. More importantly these far-reaching techs will provide meaningful and lucrative means for new StEM graduate careers of the future!

Until January then, we will leave you to ponder these thoughts and discuss thoughts that are either intriguing or questionable—please let us know. Finally, have a most joyous and relaxing holiday season. Happy 2025!

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