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PRODUCTION PROCESSES OF ROAD FUELS AND BLENDING OPTIMIZATION IN A COMPLEX REFINERY. HOW SHOULD THEY EVOLVE TO KEEP THEIR ROLE IN THE FUTURE TRASPORTATION FUEL MIXTURE.

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ΠΑΝΕΠΙΣΤΗΜΙΟ ΔΥΤΙΚΗΣ ΑΤΤΙΚΗΣ

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PRODUCTION PROCESSES OF ROAD FUELS AND BLENDING OPTIMIZATION IN A COMPLEX REFINERY. HOW SHOULD THEY EVOLVE TO KEEP THEIR ROLE IN THE FUTURE TRASPORTATION FUEL MIXTURE.

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«Είμαι συγγραφέας αυτής της μεταπτυχιακής εργασίας και ότι κάθε βοήθεια την οποία είχα για την προετοιμασία της, είναι πλήρως αναγνωρισμένη και αναφέρεται στην εργασία. Επίσης, οι όποιες πηγές από τις οποίες έκανα χρήση δεδομένων, ιδεών ή λέξεων, είτε ακριβώς είτε παραφρασμένες, αναφέρονται στο σύνολό τους, με πλήρη αναφορά στους συγγραφείς, τον εκδοτικό οίκο ή το περιοδικό, συμπεριλαμβανομένων και των πηγών που ενδεχομένως χρησιμοποιήθηκαν από το διαδίκτυο. Επίσης, βεβαιώνω ότι αυτή η εργασία έχει συγγραφεί από μένα αποκλειστικά και αποτελεί προϊόν πνευματικής ιδιοκτησίας τόσο δικής μου, όσο και του Ιδρύματος.

Παράβαση της ανωτέρω ακαδημαϊκής μου ευθύνης αποτελεί ουσιώδη λόγο για την ανάκληση του πτυχίου μου».

Επιθυμώ την απαγόρευση πρόσβασης στο πλήρες κείμενο της εργασίας μου μέχρι ……………………… και έπειτα από αίτηση μου στη Βιβλιοθήκη και έγκριση του επιβλέποντα καθηγητή.

Ο Δηλών

Γεώργιος Φουντουκάκης

Αθήνα, Νοέμβριος 2024

DECLARATION OF AUTHORSHIP

I, Georgios Fountoukakis confirm that the report entitled "**PRODUCTION PROCESSES OF ROAD FUELS AND BLENDING OPTIMIZATION IN A COMPLEX REFINERY. HOW SHOULD THEY EVOLVE TO KEEP THEIR ROLE IN THE FUTURE TRASPORTATION FUEL MIXTURE"**

is my own work. I have not copied other material verbatim except in explicit quotes, and I have identified the sources of the material clearly.

George Fountoukakis Athens, November 2024

ABSTRACT

Several debates are being circulated about the extinction of fossil fuels from the fuel basket that will be used for transportation purposes in the near future. Is this the case or with appropriate blends with bio-fuels and new techniques of new-generation fuels production, fossil fuels can still play a major play in the transportation fields for a couple of decades to come? The latter will be discussed thoroughly in the second section of this dissertation. Beforehand we'll visit the refining economics and we'll describe how refinery companies make money optimizing their gasoline and gasoil/diesel auto production, minimizing their production cost.

Thus, first chapter is devoted to gasoline blending optimization, describing in detail the construction of the optimization model along with the way to stand against the problem and the pathway to resolve it. In chapter 2 the same discussion will be held for optimizing the gasoil blending model in a modern refinery. In chapter 3 we'll delve into the substitute of gasoline for Internal Combustion Engines (ICE), which is ethanol and in chapter 4, the renewable products of biodiesel and hydro-treated vegetable oil (HVO) will be presented in extent. In last chapter the legislation in EU and US principally but also in other places of the world will be highlighted in order the reader to be aware of the forthcoming limitations of the traditional fossil road fuels and the mandates that will encourage the world to use sustainable bio-fuels for its transportation needs extensively.

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CHAPTER 1 - GASOLINE CHARACTERISTICS AND BLENDING OPTIMIZATION ANALYSIS

INTRODUCTION

Every time that we drive our gasoline moving vehicle for commuting to our job every single day or moving around covering all our needs of our routine or even whenever we get to a road trip for pleasure using our car, we hardly think beyond filling it up with fuel or the fuel price that we need to pay for.

We forget how sophisticated refinery product is gasoline and how well it performs with our car including the following characteristics:

- How well and smoothly our car engine starts up even under cold temperatures during winter time.
- How effectively engine operates providing adequate power and acceleration upon driver's demand, without annoying drawbacks known as "knocking".
- How much economy in fuel consumption can be achieved by using high quality gasoline.
- How much environmental friendly approach you attain using high quality fuel that releases low emissions out of its combustion.
- How well performs within the machinery environment of the car engine without adding deposits to the engine or contaminate or corrode vehicle's fuel system and exhaust system.

But how gasoline can achieve all the above expectations and at the same time to comply with the stricter and stricter specifications for low emissions that US and EU are imposing? This is the sophisticated engineering of the oil blending processes of a modern refinery that we'll discuss in wide extent in the first section of this dissertation.

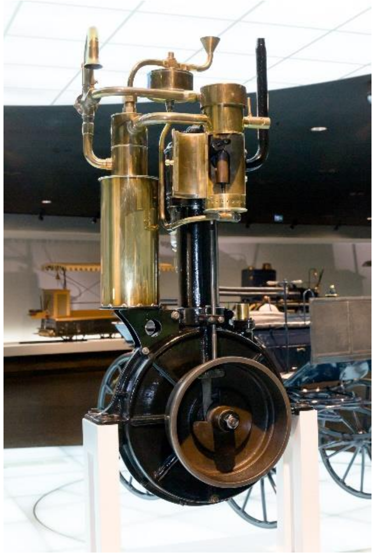
The first 70 feet deep crude oil well was discovered – literally was dug – back in 1859 by Edwin Drake and his principal target was to distill oil and produce kerosene for lighting purposes. The major product wasn't gasoline; it was lamp oil, called coal oil or kerosene. People were reading more and more and they wanted better light than that provided by candles and whale oil lamps. Out of the distillation, gasoline and other products were also produced but being so volatile to use in lamps, Drake disregarded them, until the first Otto engines were invented in Germany. The development of electric light and the astonishing popularity of the automobiles in the first decades of the 20th century, turned the industry's focus from kerosene to gasoline. In 1922 gasoline sales exceed kerosene's sales for the first time.

In about twenty years after Drake's first well discovery, the first Nikolaus Otto-engines invention stimulated the development of internal-combustion engine using the "carburetor" as a means of introducing fuel into combustion chamber. Ideally the fuel mixture requires only about 6-7% of petroleum vapor mixed with air. The carburator provides the means of achieving this in a controlled consistent way. In particular, in May 1876 Nicolaus Otto produced designs for the 4-stroke engine. Those designs were developed from steam and gas engines but Otto made use of the availability of a combustible liquid fuel.

Picture 1 The three wheeler (tricycle) designed by Benz

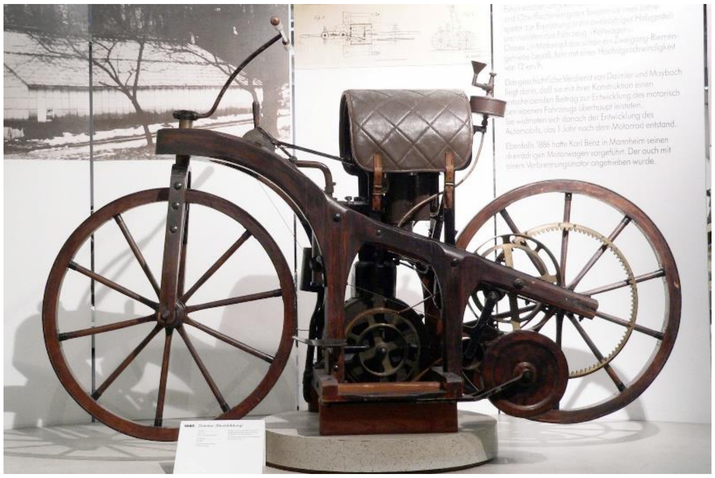
His two rivals, great engineers though, Gottlieb Daimler (1834-1900) and Carl Friedrich Benz (1844-1929) disputed his claims to be the first inventor of motor car. The vehicle designed by Benz was a tricycle, a three wheeler, which was patented and operated in Germany in 1886. Benz's tricycle was powered by an 1,0 lit (954 cc) single cylinder Otto type engine, mounted on it, with an output of two thirds of a horsepower (hp). As fuel was used a kind of gasoline, called ligroin (invented as laboratory solvent, sort of naphtha).

Daimler made use of the engines in a variety of ways. Working with Wilhelm Maybach in 1884, he develops an internal combustion engine known today as the 'Grandfather Clock'. He successfully installed that engine in a four-wheeled carriage and later based on “Grandfather Clock” he designed a motor launch. Actually, in the summer of 1886, Daimler equipped three different-sized boats with this small and powerful engine. The “Neckar”, the biggest of the three, taken his name after the river where it was cruising while testing, was offering space for up to ten people. “Neckar” was moving using the engine, on which Daimler and Maybach had been working since 1882 in Cannstatt and which they first launched in the two-wheeled ‘Reitwagen’ (the first internal combustion motorcycle) in 1885. This craftsmanship was proved to be highly successful and brought Daimler in contact with the early British Petroleum Refiners. He was looking for a suitable spirit of the gasoline type for use as a fuel for his launch engine.



Picture 2 The 1885 “Grandfather Clock” Engine as being exhibited at Mercedes-Benz Museum

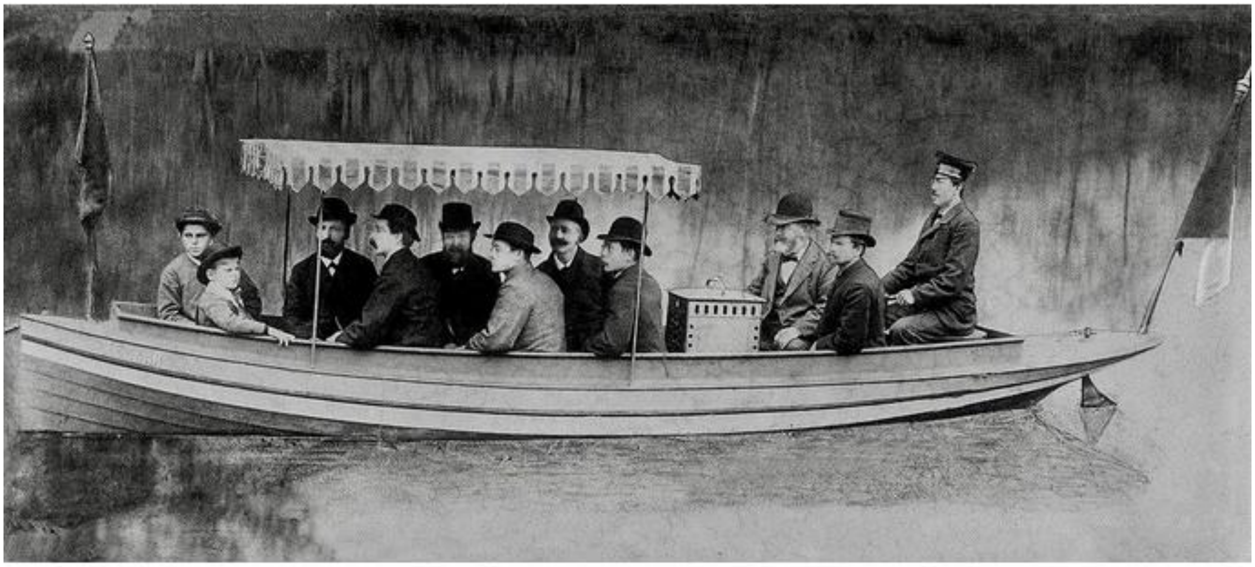
Photo by Morio - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/



Picture 3 The Reitwagen (riding car), the first internal combustion motorcycle (1885)

Photo by Joachim Köhler - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/

Gasoline octane and lead levels increased over time. By the 1950s cars were becoming bigger and faster. Gasoline octane increased and lead was added to improve engine's performance. Lead was broadly accused for rising air pollution with harmful effects to humans, animals and plants. Therefore, leaded gasoline was taken off the US market. Unleaded gasoline was introduced in the 1070s when health problems caused from lead became common. In the US leaded gasoline for use in on-road vehicles was completely phased out as of 1st January 1996 (eia.gov). Likewise, in Europe, Germany was the first EU-member which raised concerns about use of lead in gasoline, passing reduction regulations as early as in 1971. It was not until 1985 that the EU obliged its members, by law, to introduce Super Unleaded (95 octane) to their markets, from 1st October 1989, while the supply of unleaded gasoline (92 octane) remained voluntary. In 1986, several EU members implemented the supply of unleaded gasoline. Moreover, in 1987 all EU members were allowed to prohibit the production and use of leaded gasoline (92 octane) (osti.gov).



Picture 4 In August 1886, Gottlieb Daimler and Wilhelm Maybach (sitting on either side of the engine housing) undertook the first test drives with Daimler motorboats on the Neckar River

Source: Mercedes-Benz Classic archives photos

Next milestone in gasoline's use history is the time that Ethanol is added to gasoline. In 2005 the US Congress enacted a Renewable Fuel Standard (RFS) that set minimum requirements for use of renewables, including ethanol in motor fuels. In 2007 the RFS targets were to rise steadily to 36 billion gallons by 2022. In 2021 about 13,5 billion gallons of ethanol were added to motor gasoline in the US. In most of US the retail finished motor gasoline is about 10% ethanol by volume. On the other side Europe imports Ethanol because its production doesn't suffice to cover the demand. In particular, annually, Europe produces abt 9 billion litres of ethanol, with 2,0 billion litres originated by French farming sector and 2,0 billion litres been imported; mainly coming from Pakistan, USA and Brazil (data of year 2022, epure.org).

Gasoline also called gas or petrol is a mixture of volatile flammable liquid hydrocarbons derived from petroleum and used as a feed in the internal-combustion engines (ICEs). It can also be used as a solvent for oils and fats. Originally, gasoline became the preferred automobile fuel due to its high energy of combustion and its capacity to get mixed easily with air in the “carburetor” of first passenger cars.

Gasoline is a mixture of hundreds of different hydrocarbons which have been mixed in the refining industry to meet a set of engine performance specifications and many different compositions are possible. The performance specifications vary with season, requiring more volatile blends during winter to be able to start a cold engine. At the refinery the composition varies according to the crude oils from which it is produced, the type of processing units that a refinery complex operates and the blending streams that each refinery opts to use when blending the final product. The bulk of a typical gasoline consists of a homogeneous mixture of lightweight hydrocarbons, between 4 and 12 carbon atoms per molecule. It’s a mixture of paraffins (alkanes), olefins (alkenes) and cycloalkanes (naphthenes). The actual ratio of aforesaid molecules depends on:

- The refinery that produces the material, as not all refineries have the same set of processing units
- The crude oil slate used by the refinery
- The grade of the gasoline, particularly the octane rating

In a modern refinery we can meet several different process streams that need to be handled. These streams are originated from the entire range of processing units; from the crude distillation units under atmospheric pressure and/or under vacuum, the most basic units of a refinery, till the most sophisticated units of Fluid Catalytic Cracking (FCC) and Hydro-cracking/Hydro-processing. Gasoline is a complex mixture of hydrocarbons having boiling points in the range of 30°C – 215°C. It contains paraffins, olefins, naphthenes and aromatics and it was originally discarded as a by-product of kerosene production. But due to its ability to vaporize at low temperatures it used to be useful as a fuel for several machinery equipment. Gasoline was initially produced by atmospheric distillation but the product was of low quality, with regard to Research Octane number (RON), which is an indication of the knock resistance of the gasoline in engines and other attributes. This flaw drove increased research into production of gasoline from other less commercial refinery products in several chemical processes and an attendant improvement in refinery complexity. In addition the ongoing significant increase in demand addressed the refiners to ensure that the product will be available in the demanded volume ensuring that its quality and specifications needed for effective performance will not be compromised.

BASIC ATTRIBUTES OF GASOLINES

We can recognize the following critical attributes – in terms of quality requirements - of gasolines:

1. Adequate quality to be combusted properly (Octane Number)

The transition of flame from the spark plugs to the entire combustion chamber effects to high temperatures and pressures resulting to pre-flame reactions of fuel. If these reactions are scaled up, the fuel can be auto-ignited with “knocking” effect to be appeared. The shock wave creates the characteristic metallic "pinging" sound, and cylinder pressure increases dramatically. Effects of engine knocking range from inconsequential to completely destructive. The higher the octane number the smoother flame’s expansion minimizing the above undesired effect.

The tendency of gasoline to appear “knocking” effect is related to:

- The design of internal combustion engine (compress ratio, air/fuel ratio, cooling system)
- The operating conditions of the engine (effect tends to be higher in more severe working conditions)
- The environmental conditions around the engine (effect appears to be higher in more intense pressure and temperature conditions)
- The chemical composition of gasoline

In the latter we can refer further as low “knocking” effect derives from aromatics (like toluene), high-branched iso-paraffins, olefins (like di iso-butylene). Medium “knocking” effect is related to cycloalcanes (like cyclohexane), low-branched iso-paraffins and high “knocking” effect is related to normal parafines (like n-heptane, etc). Schematically, the above is illustrated in figure 5.

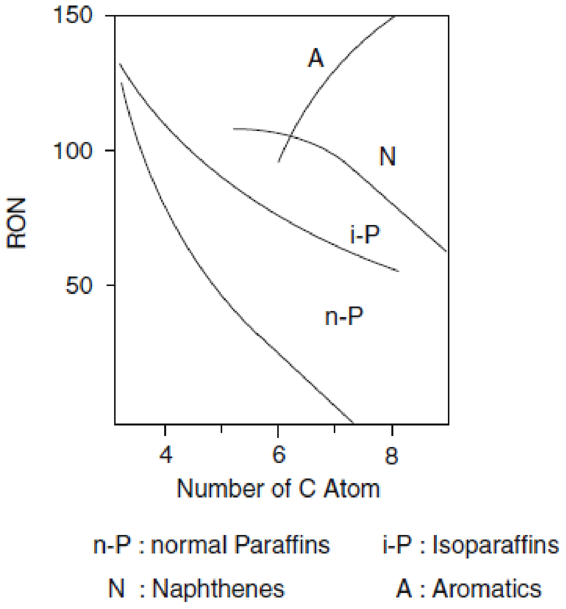


Figure 1 "Knocking" effect related to paraffin content

The Octane Number is the content of iso-octane is a mixture of iso-octane and heptane that corresponds to the same “knocking” performance with the under testing fuel sample. It is measured by Research Octane Number (RON) and Motor Octane Number (MON). The RON test is run in a standard one-cylinder CFR (Co-operative Fuel Research) engine at a speed of 600 rpm and an intake temperature of 52 ^{o}C, while the MON test is run at 900 rpm with higher intake temperature of 149 ^{o}C. These tests are run under strict, well defined procedures. The octane scale is based on two alkanes, n-heptane (octane number = 0) and iso-octane (octane number = 100). The blends of these components are referred to as primary reference fuels (PRF) and define the intermediate points in the RON or MON scale. The RON or MON is the volume percent of iso-octane in the PRF. Thus a blend of 90 vol% iso-octane and 10 vol% n-heptane is assigned the octane number of 90 in both RON and MON scales. A fuel is assigned the RON (or MON) value of the PRF that matches its knock behavior in the RON (or MON) test. All practical gasolines are mixtures of aromatics, olefins, naphthenes, oxygenates, and alkanes. A practical gasoline will match the PRF of a higher octane number in the RON test and hence has a higher RON when compared to the MON test. The difference between RON and MON is known as the sensitivity.

2. Certain volatility (Reid Vapor Pressure - RVP)

Gasoline needs to be that much volatile to allow easy engine start-up, integrated warm-up of the metallurgy until engine reaches the normal operating temperature and consistent fuel distribution to the total of cylinders of the engine. At the same time gasoline doesn’t need to be that much volatile to produce vapor lock effect, carburetor icing effect or leakage due to evaporation.

When gasoline vapor pressure is low, the engine may have to be cranked for a while before it gets started. On the other hand, when vapor pressure is extremely low, the engine may not start at all. Higher values of vapor pressure perform better in cold-start conditions, but lower values are better to prevent vapor lock and other hot fuels handling problems.

Vapor lock and hot fuel handling problems occurs when excessive gasoline vapor accumulates somewhere in the fuel system and reduces or interrupts the fuel supply of the engine. This may occur in the fuel pump, the fuel line, the carburetor or the fuel injector. When the fuel supply is reduced, the air-fuel ratio become too lean on fuel (too much air to the proportion of fuel injected), which may cause loss of power, surging, or back-firing. When the fuel supply is interrupted, the engine stops and it’s difficult to restart until the fuel system has cooled and the vapor has condensed.

Carburetor icing occurs when intake air is chilled below the freezing point of water by evaporation of gasoline in the carburetor. Ice forms on the throttle blade and in the venture and can interrupt the carburation, resulting in engine stall. Icing can be acute when the air is moist (70% or higher relative humidity) and the ambient temperature is between 2^oC and 13^oC. Carburetor icing is not a problem when the intake temperature is below freezing because the air is too dry.

Vapor lock index (VLI) is used to control vapor lock and other hot fuel handling problems. VLI is calculated using vapor pressure in kPa and distillation profile percent evaporated at 70°C (158°F), as follows:

$VLI = 10(VP) + 7(E70)$

VLI varies with the season. The normal range is 800 to 1250. Lower values provide greater protection against vapor lock and hot fuel handling problems.

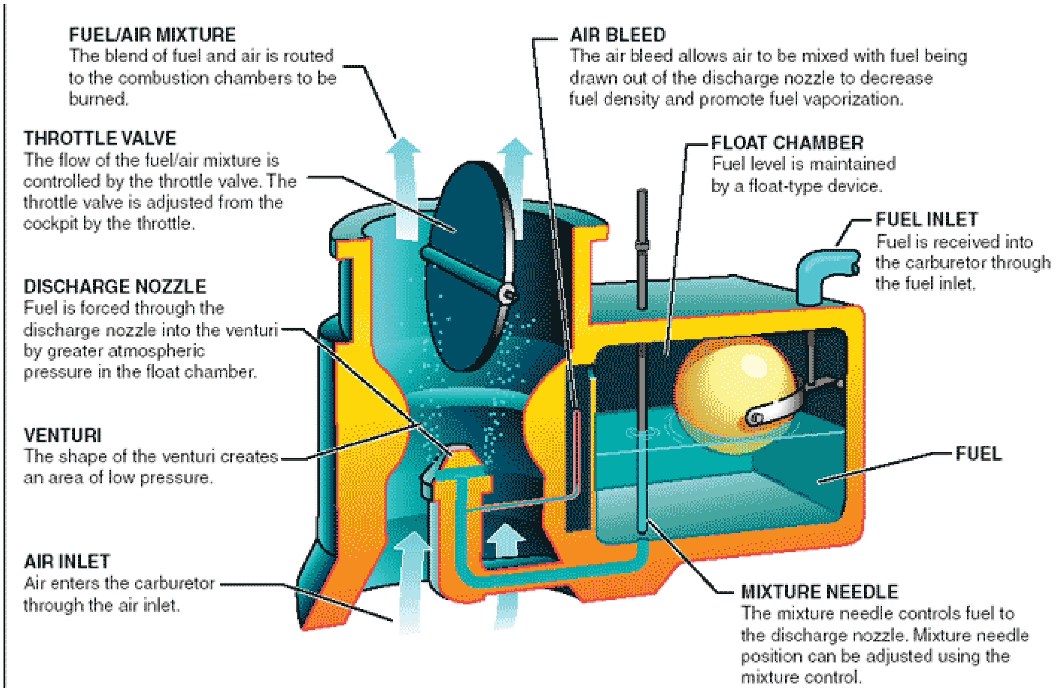


Figure 2 Carburetor and its parts

3. Product Stability & Consistency

A fuel that undergoes oxidation, polymerization, or other reactions in the liquid phase that alter its composition, has chemical instability. The chemical reactions of oxidation or polymerization can produce generally higher molecular-weight compounds that are insoluble in the fuel, such as lacquers, gums, and solids. These species are called deposits if they adhere to fuel-system, in-cylinder, or other engine components. Such deposits can plug fuel filters, prevent proper injector operation, foul in-cylinder components like piston rings and valves, and increase engine emissions.

4. Material compatibility resulting to non-corrosive behavior

A fuel is called to be corrosive to a given metal if it chemically reacts with and degrades the surface quality of the metal over time at prevailing conditions under normal operation of the system. Gasoline needs to be non-corrosive for proper storage behaviors in petrol stations’ tank farm and car fuel tanks alike. Fuel’s corrosiveness is commonly quantified using a test method in which a polished strip of copper is submerged in the fuel at an elevated temperature for several hours and then visually compared to reference strips. Sometimes a silver strip is used in place of copper because many fuel-level sensors contain silver.

5. Composition

Gasoline needs to meet certain requirements connected to its composition. Benzene content needs to be lower than 1% due to its toxic attribute, aromatics need to be controlled as they are pollutants for the environment, oxygenates (bio-ethers and/or bio-alcohols) need to be used at certain extent in order not to harm engines, sulphur content is limited by legislations (e.g. EU directives) at max 10%.

THE BLENDING PROBLEM – DESCRIPTION

Gasoline blending is the mechanical mixing of gasoline blending components streams to obtain various grades of gasoline. In our problem we need to produce four (4) types of gasoline:

1. Unleaded 95Ron – bio for domestic market
2. Unleaded 98Ron – bio for domestic market
3. Unleaded 100Ron – bio for domestic market
4. Unleaded 95Ron – bio-free for exports

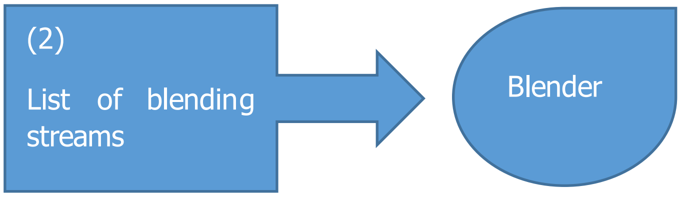
(1)

List of final products

In the domestic market according to State’s legislation the supplied gasoline must be a mixture with pure ethanol or ethers produced by ethanol of biological origin in a concentration of 3,3%. This mandatory attribute applies to the whole range of gasolines produced and supplied in the domestic market (95ron, 98ron, 100ron). This concentration is a parameter of the problem since it can be changed by law at any time. The market prices that final products can be sold are also parameters of the problem since the market is dynamic and prices can be changed significantly from one time period to the other. It’s also worth mentioning that the product goes for export is bio-free due to its intentioned destination. On one hand, this product needs to be priced competently to be sold in the international markets, on the other hand there is no bio-gasoline mandate in place over these markets (like Turkey, Libya, Egypt, Algeria, etc). For that instance ETBE will be used as an octane booster for domestic market and MTBE for export volumes. ETBE is produced from bio-ethanol treatment within the refinery, but ethanol as feedstock is imported. On the other hand, MTBE can either be produced in-house out of methanol treatment or it can be imported, at a higher cost.

In a highly complex refinery the most commonly employed streams in gasoline production are presented below:

1. FCC naphtha
2. Isomerate
3. Light Naphtha (LSR)
4. Reformate
5. Heavy Naphtha (TRN)
6. Butane – C4
7. MTBE
8. ETBE
9. Alkylate



Therefore the blending problem comprises the blending of above streams to that extent that the objective function of overall revenue of the sale of final products minus the cost of above blending streams will be maximized.

The base for our calculations will be the monthly demand in volume (Cubic Meters - M^3) or mass (Metric Tons - MT) and monthly availability of blender's feed streams respectively.

Then, we can declare the below **variables of the problem**:

X(ij) the quantity of stream i blended in product j

where i ranges from 1 to 9 as per above listing of feed streams (2)

and j ranges from 1 to 4 as per above listing of final products (1)

Y(j) the quantity of j final product

where j ranges from 1 to 4 as per above listing of final products (1)

We can write the objective function as per below:

$\Sigma Y(j)*P(j) - \Sigma X(ij) * C(i) \rightarrow \max$

where P(j) is the unit price that final product Y(j) is sold

and C(i) is the unit price that each blending stream costs

At this stage of analysis we need to evaluate accurately the cost per mass or volume unit of each blending stream. We need to distinguish between the streams that are getting imported in the system and they are purchased at a market price and those which are originated from the refinery's processes and need to be assigned a realistic value-cost. This is a wide discussion that needs to be exploited in detail here below.

Subject to several constraints:

a) Properties / Specifications of final products constraints
b) Availability of blending streams constraints
c) Storage constraints of blending streams
d) Final products demand constraints
e) Storage constraints of final products
f) Mass balance on blender processing unit

The second important issue that needs to be determined is the critical attributes of the final products (like RON/MON, density, Vapor Pressure, Sulphur content, Aromatics content, Olefin content, Oxygenate content, etc) that will be included in category (a) of constraints as stated above. In addition we should take into account that some of those attributes are linear while mixing different streams and others are not getting mixed in a linear manner. Therefore in the latter case we need to search in bibliography and determine appropriate rules-equations to correlate the properties of the mixing components like they were getting mixed in a linear way. This is also a very challenging task of our gasoline blending problem.

The demand of the products can be classify in three main categories:

1. The demand for domestic market that usually is the principal market for a refinery with the higher margins. It's certainly non-economic for a company to import in the country ready products whereas a refinery operates in the bounds of the reference country. This is explained due to the high freight costs expected to be incurred in the final price of the imported goods that make them more expensive compared to the in-country refined and produced goods.
2. The demand for intermediate materials that a refinery uses in its internal refining and treating operations between the several units. The production cost of the intermediates needs to be kept in low levels to utilize the production of final goods in terms of cost.
3. The demand of the surplus quantity of goods needs to be stored and exported in neighbor countries and enhance further refinery's revenue.

In our case we will target three gasoline products that the refinery company opt to market:

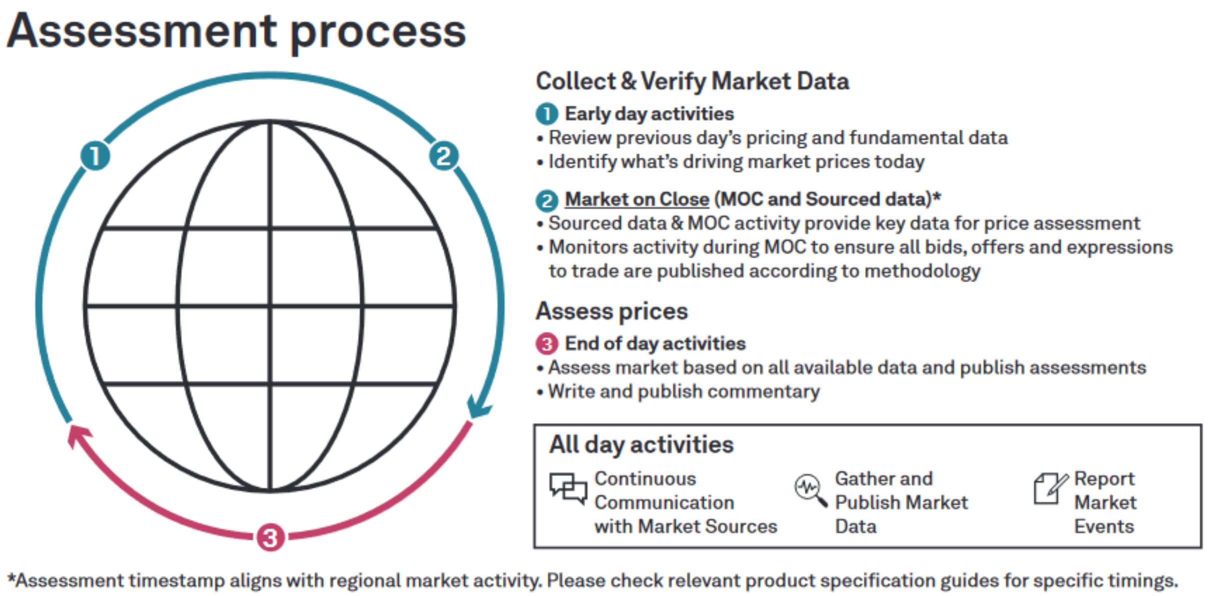
1. Unleaded 95Ron for domestic market
2. Unleaded 98Ron for domestic market
3. Unleaded 100Ron for domestic market
4. Unleaded 95Ron for exports

The refined oil products - either semi-ready or intermediates that are been traded between refineries to be enhanced and treated further for delivering final products or ready-to-use products – have not the same price in the markets. In addition there is no single, universal market either. First, we have to recognize different markets in terms of their geographical position with their own characteristics and prevailing conditions. For example African countries produce crude oil but they import final products due to shortfall in refining capacity. Some regions lack certain products, for example Europe is short in ethanol, as we will analyze later, and they are long in other oil products. Other markets are quite balanced in certain product categories (heavy distillates, fuel oil, bitumen) and might be well unbalanced in other type of products (light ends, lpg, gasolines). In addition we should take into consideration the environment in terms of political instabilities, war conflicts, sabotaging of pipe transfer operations or oil drilling operations, damages in infrastructure critical for the movement of oil and uninterrupted supply arrangements in a certain territory. Even the effect of climate change or the adverse weather conditions at specific areas that might be vulnerable to that kind of instabilities and dangers, should be taken into account to evaluate a certain market.

The base prices that entire oil industry uses as benchmark prices to trade on, is the Platt’s Price Publications released by S&P Global Inc. It’s an American publicly traded corporation headquartered in Manhattan, New York City. Its primary areas of business are financial information and analytics. Platt’s methodologies are designed to produce price assessments that are representative of market value and of the particular markets to which they relate. Platt’s methodologies have evolved to reflect changing market conditions through time. Company’s analysts and reporters are in constant communication with the market players, sellers and buyers throughout continent and gather information on the grounds of the trades that are truly fulfilled. They consider several criteria as to whether to use source information, like:

- Company reputation
- Source position within the company
- Source understanding and knowledge of the market in question
- Ability of source to provide relevant, valuable information
- Other data that may be relevant to Platt’s assessment

Company’s reporters are entitled to cover the markets of Asia and Middle East, Europe and Africa and also America. They’re all reachable during several time intervals related to the time zone of the market they cover.



Assessment process

Collect & Verify Market Data

1 Early day activities
- Review previous day's pricing and fundamental data
- Identify what's driving market prices today

2 Market on Close (MOC and Sourced data)*
- Sourced data & MOC activity provide key data for price assessment
- Monitors activity during MOC to ensure all bids, offers and expressions to trade are published according to methodology

Assess prices

3 End of day activities
- Assess market based on all available data and publish assessments
- Write and publish commentary

All day activities

Continuous Communication with Market Sources | Gather and Publish Market Data | Report Market Events

*Assessment timestamp aligns with regional market activity. Please check relevant product specification guides for specific timings.

Figure 3 Price Assessment Process by International Firms

Another company publishes price assessments daily, is Argus. Argus is a privately held UK-registered company, which produces price assessments and analysis of international energy and other commodity markets and also offers consulting services and conferences.

PRICE STRUCTURE

The price of the product is calculated on the unit quantity by volume or mass. Therefore the price will be recorded in US dollars per metric ton or US dollars per cubic meter. It might be listed in other currencies also, depending on the geographical area that the majority of trades are registered. The unit price of a product is composed by two elements. First is the Platt's quote, the market assessment of specific product for the specific geographical region. This quote is published daily by Platt's or Argus Organization, as discussed above. Therefore every product has an inherent different price from day to day. The second element that structures the price is the premium or discount imposed on the base price. The two elements sum up to the final unit price of the product. This price fluctuates daily, because the market does not correspond to a steady state but reflects a dynamic environment that many things can happen from one day to the other that can amend the balance between the supply and demand for a specific product within a specific region. For example disruption in supply may happen due to hiccups in region refineries production. More extreme events could be reported, which would trigger unbalances in supply and demand, like the outburst of a war or the sabotaging of crude oil wells in a certain region, usually in Africa or Middle East or Latin America, in generally in certain politically uncertain countries of the world.

The oil industry trades widely crude oil, a quite extended variety of crudes, depending upon their exploration site and their properties and oil products, gasoline and diesel auto among them. Oil refining companies, oil trading houses, oil trading brokers, ship owners, tanker charterers or any other stakeholder in the oil supply chain, in principal, they use the Incoterms rules to materialize their trade agreements and physical shipments. Incoterms rules are a set of standards, established by International Chamber of Commerce (ICC), used in international and domestic contracts for delivery of goods. First published by ICC in 1936, Incoterms rules provide internationally accepted definitions and rules of interpretation for most common commercial terms used in contracts for the sale of goods. Developed and maintained by experts and practitioners Incoterms have become the standard in international business rules setting, recognized by the United Nations Commission on International Trade Law (UNCITRAL) as the global standard for the interpretation of the most common terms in foreign trade.

The most common Incoterms used in oil trading are:

- Ex Works (EXW): This rule places minimum responsibility on the seller, who merely has to make the goods available, suitably packaged, at the specified place, usually the seller’s factory or depot.
- Free Carrier (FCA) or
  Free On Board (FOB): This is a very flexible rule, suitable for all situations where the buyer arranges the main carriage. Seller arranges pre-carriage from seller’s depot to the named place, which can be a terminal or transport hub, forwarder’s warehouse etc. Delivery and transfer of risk takes place when the truck or other vehicle arrives at this place, ready for unloading. The carrier is responsible for unloading the goods.

  In the case that goods are transported by sea or inland waterway Free On Board (FOB) should be used instead.

- Cost Insurance and Freight (CIF): Use of this rule is restricted to goods transported by sea or inland waterway. Seller arranges and pays for transport to named port. Seller delivers goods, cleared for export, loaded on board the vessel. However risk transfers from seller to buyer once the goods have been loaded on board, i.e. before the main carriage takes place. Seller also arranges and pays for insurance for the goods for carriage to the named port.

FOB VS CIF BASIS PRICE LISTING

Price listing for oil products is addressed to the geographical site that a trade is taking place. That's why Platt's (or Argus) publish one price quote for one unique product (e.g. Gasoline Premium Unleaded 95Ron) for one region, e.g. Mediterranean basin and another price quote for the same product for North West Europe (NWE) zone for the same day. Price assessments are released daily and be updated every working/trading day, as explained before. Surely, there might be similar products (gasolines for example) with similar but not identical attributes in different continent zones. These quality requirements might be imposed by certain climate conditions (for example pour point and cold filter plugging point on diesel auto) or group of countries' legislation. In that case, the price assessment will be surely different as the two similar gasolines will be treated by the researcher as different products.

Further to the different price listing in terms of location of trading, oil products are assessed differently in terms of Incoterms rule of delivery used under fulfilled trade. That's why for the same, unique product (e.g. Gasoline Premium Unleaded 95Ron) for the Mediterranean market one quote is attributed to an FOB transaction and one different quote is endorsed to a CIF shipment for the same trading day. The difference in the price of two quotes should normally designate the prevailing freight cost (along with the insurance cost but that's really small) to deliver this specific product to a depot in the geographical zone of the assessment.

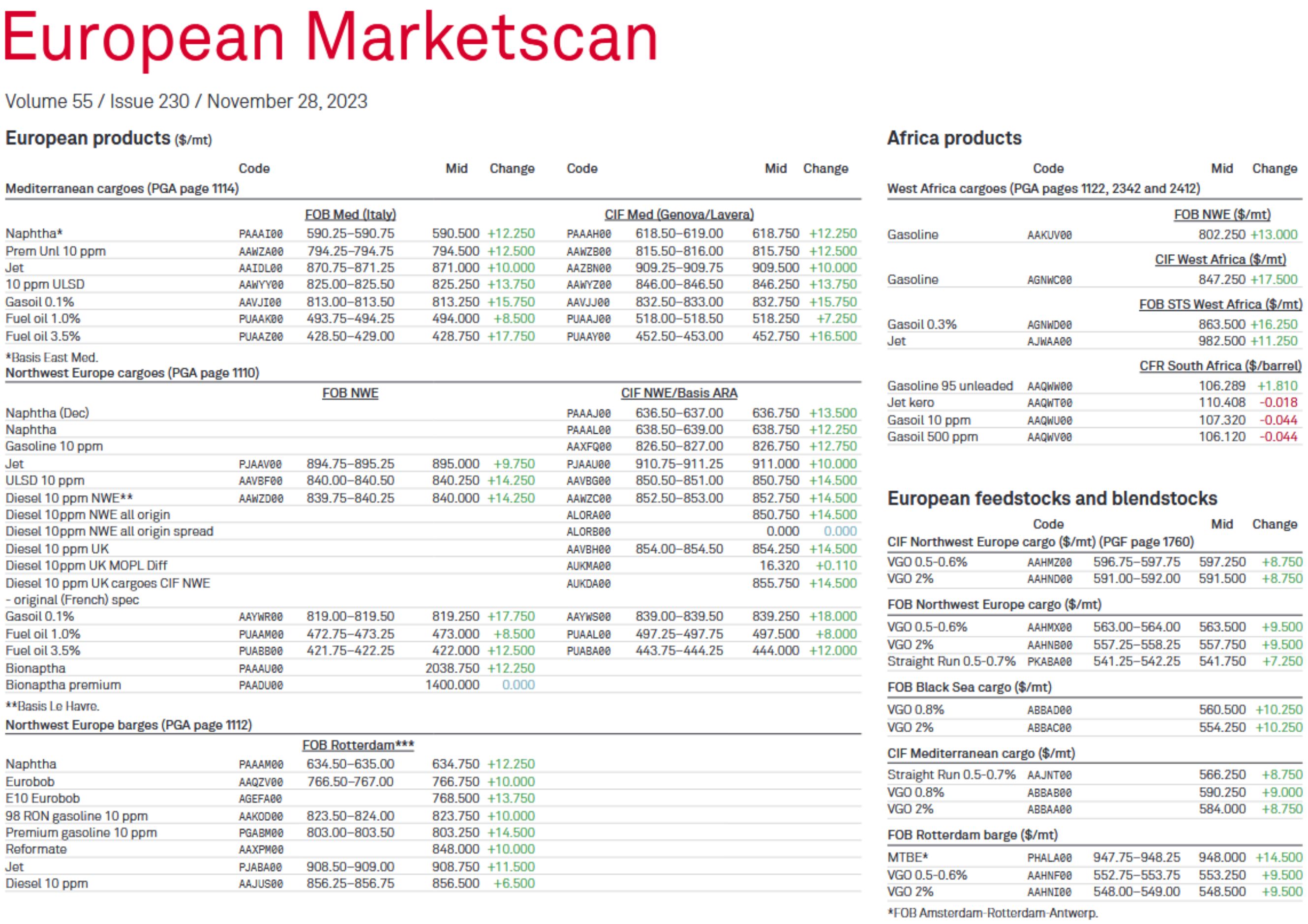
THE MEANING OF "ARBITRAGE"

We use the term "arbitrage" or more precisely the phrase "arbitrage is open from one geographical area to another" (for instance from US to Europe) to describe the opportunity that is caused - under certain circumstances - the product produced in US not to be sold in US but to be delivered to European market instead. This can happen when the Platt's reference price of the material in

Europe plus the transportation cost from US to Europe exceeds the Platt's reference price of the material in US market, where it was produced. Of course, it is well understood that "arbitrage is open" for certain periods but it gets closed during other time intervals, depending upon the prevailing market conditions on the two different districts under discussion and certainly depending on the fluctuation of the transportation cost from place to place.

An example of Platt's publication is the following:

Table 1 Platt's Marketview snapshot



European Marketscan

Volume 55 / Issue 230 / November 28, 2023

European products ($/mt)

	Code		Mid	Change	Code		Mid	Change
Mediterranean cargoes (PGA page 1114)								
		FOB Med (Italy)				CIF Med (Genova/Lavera)		
Naphtha*	PAAAI00	590.25–590.75	590.500	+12.250	PAAAH00	618.50–619.00	618.750	+12.250
Prem Unl 10 ppm	AAWZA00	794.25–794.75	794.500	+12.500	AAWZB00	815.50–816.00	815.750	+12.500
Jet	AAIDL00	870.75–871.25	871.000	+10.000	AAZBN00	909.25–909.75	909.500	+10.000
10 ppm ULSD	AAWYY00	825.00–825.50	825.250	+13.750	AAWYZ00	846.00–846.50	846.250	+13.750
Gasoil 0.1%	AAVJI00	813.00–813.50	813.250	+15.750	AAVJJ00	832.50–833.00	832.750	+15.750
Fuel oil 1.0%	PUAAK00	493.75–494.25	494.000	+8.500	PUAAJ00	518.00–518.50	518.250	+7.250
Fuel oil 3.5%	PUAAZ00	428.50–429.00	428.750	+17.750	PUAAY00	452.50–453.00	452.750	+16.500

*Basis East Med.

	Code		Mid	Change	Code		Mid	Change
Northwest Europe cargoes (PGA page 1110)								
		FOB NWE				CIF NWE/Basis ARA		
Naphtha (Dec)					PAAAJ00	636.50–637.00	636.750	+13.500
Naphtha					PAAAL00	638.50–639.00	638.750	+12.250
Gasoline 10 ppm					AAXFQ00	826.50–827.00	826.750	+12.750
Jet	PJAAV00	894.75–895.25	895.000	+9.750	PJAAU00	910.75–911.25	911.000	+10.000
ULSD 10 ppm	AAVBF00	840.00–840.50	840.250	+14.250	AAVBG00	850.50–851.00	850.750	+14.500
Diesel 10 ppm NWE**	AAWZD00	839.75–840.25	840.000	+14.250	AAWZC00	852.50–853.00	852.750	+14.500
Diesel 10ppm NWE all origin					ALORA00		850.750	+14.500
Diesel 10ppm NWE all origin spread					ALORB00		0.000	0.000
Diesel 10 ppm UK					AAVBH00	854.00–854.50	854.250	+14.500
Diesel 10ppm UK MOPL Diff					AUKMA00		16.320	+0.110
Diesel 10 ppm UK cargoes CIF NWE - original (French) spec					AUKDA00		855.750	+14.500
Gasoil 0.1%	AAYWR00	819.00–819.50	819.250	+17.750	AAYWS00	839.00–839.50	839.250	+18.000
Fuel oil 1.0%	PUAAM00	472.75–473.25	473.000	+8.500	PUAAL00	497.25–497.75	497.500	+8.000
Fuel oil 3.5%	PUABB00	421.75–422.25	422.000	+12.500	PUABA00	443.75–444.25	444.000	+12.000
Bionaptha	PAAAU00		2038.750	+12.250				
Bionaptha premium	PAADU00		1400.000	0.000				

**Basis Le Havre.

	Code		Mid	Change
Northwest Europe barges (PGA page 1112)				
		FOB Rotterdam***		
Naphtha	PAAAM00	634.50–635.00	634.750	+12.250
Eurobob	AAQZV00	766.50–767.00	766.750	+10.000
E10 Eurobob	AGEFA00		768.500	+13.750
98 RON gasoline 10 ppm	AAKOD00	823.50–824.00	823.750	+10.000
Premium gasoline 10 ppm	PGABM00	803.00–803.50	803.250	+14.500
Reformate	AAXPM00		848.000	+10.000
Jet	PJABA00	908.50–909.00	908.750	+11.500
Diesel 10 ppm	AAJUS00	856.25–856.75	856.500	+6.500

Africa products

	Code	Mid	Change
West Africa cargoes (PGA pages 1122, 2342 and 2412)			
		FOB NWE ($/mt)	
Gasoline	AAKUV00	802.250	+13.000
		CIF West Africa ($/mt)	
Gasoline	AGNWC00	847.250	+17.500
		FOB STS West Africa ($/mt)	
Gasoil 0.3%	AGNWD00	863.500	+16.250
Jet	AJWAA00	982.500	+11.250
		CFR South Africa ($/barrel)	
Gasoline 95 unleaded	AAQWW00	106.289	+1.810
Jet kero	AAQWT00	110.408	-0.018
Gasoil 10 ppm	AAQWU00	107.320	-0.044
Gasoil 500 ppm	AAQWV00	106.120	-0.044

European feedstocks and blendstocks

	Code		Mid	Change
CIF Northwest Europe cargo ($/mt) (PGF page 1760)				
VGO 0.5-0.6%	AAHMZ00	596.75–597.75	597.250	+8.750
VGO 2%	AAHND00	591.00–592.00	591.500	+8.750
FOB Northwest Europe cargo ($/mt)				
VGO 0.5-0.6%	AAHMX00	563.00–564.00	563.500	+9.500
VGO 2%	AAHNB00	557.25–558.25	557.750	+9.500
Straight Run 0.5-0.7%	PKABA00	541.25–542.25	541.750	+7.250
FOB Black Sea cargo ($/mt)				
VGO 0.8%	ABBAD00		560.500	+10.250
VGO 2%	ABBAC00		554.250	+10.250
CIF Mediterranean cargo ($/mt)				
Straight Run 0.5-0.7%	AAJNT00		566.250	+8.750
VGO 0.8%	ABBAB00		590.250	+9.000
VGO 2%	ABBAA00		584.000	+8.750
FOB Rotterdam barge ($/mt)				
MTBE*	PHALA00	947.75–948.25	948.000	+14.500
VGO 0.5-0.6%	AAHNF00	552.75–553.75	553.250	+9.500
VGO 2%	AAHNI00	548.00–549.00	548.500	+9.500

*FOB Amsterdam-Rotterdam-Antwerp.

It's time to refer to the price determination of the above products. The base price is the price of Unleaded 95Ron. There is a premium on top of the 95Ron referring to 98Ron and 100Ron because there are more enhanced gasoline types with higher Octane Number. That means that the production cost for a refinery is higher compared to plain gasoline type. In addition, the market of those "advanced" gasolines imposes higher rates because corresponding market targets drivers possessing more expensive cars, equipped with high displacement engines - frequently they possess sports cars/super cars – and they are eager to pay more for their fuel. They believe that paying more on advanced fuel they reserve the "healthy" behavior of their car's engine, effecting in less future mechanical damages and lower maintenance cost.

Table 2. Price allocation to final products

product	**base price Prem Unl 10ppm FOB Med (Italy) $/mt**	**differential $/mt**	**total price $/mt**
Unleaded 95 domestic	795	70	865
Unleaded 98 domestic	795	110	905
Unleaded 100 domestic	795	150	945
Unleaded 95 export	795	20	815

The price determination of blending streams takes place regularly. Daily assessment or monthly moving average of Platt's quotes can be used. The Optimization Department of the refinery requests feedback update from the Supply and Trading division on below differential values every week or every second week. In this way the optimized production plan can be revisited regularly and be tuned accordingly to embrace the latest conditions of the market/environment that the refinery operates. Usually in the beginning of the month M-1 the production planning modelling is set and by using the average prices of about first 10 or 15 days the refinery production optimization model is executed and the production framework is determined for the month M. Then, the model is revisited frequently, as described above, to keep in line with the fluctuation of the prices or the diversification of forecasts in demand/sales of final products.

Table 3. Price allocation to blending streams

stream	Platt's assessment reference	base price $/mt	differential $/mt	total price $/mt
fcc naphtha	Prem Unl 10ppm FOB Med (Italy)	795	5	800
isomerate	Prem Unl 10ppm FOB Med (Italy)	795	50	845
lsr	Naphtha FOB Med	590	5	595
reformate	Prem Unl 10ppm FOB Med (Italy)	795	50	845
trn	Naphtha FOB Med	590	-20	570
butane	Butane FOB Med	620	-100	520
mtbe	Mtbe barges FOR Rot	948	50	998
etbe	Mtbe barges FOR Rot	948	300	1.248
alkylate	Prem Unl 10ppm FOB Med (Italy)	795	200	995

- The FCC naphtha is one of the products of catalytic pyrolysis (Fluidized Catalytic Cracking – FCC Unit).

Table 4. Basic distillate streams characteristics

Product	Boiling Range (oC)	Yield (%wt)	Usage
Lpg	C1 – C4	25~30	Alkylation Unit Feed Polymerization Unit Feed Gas fuel for refinery
Naphtha (FCC)	C5 - 220	50~60	Gasoline blender
Light Cycle Oil (LCO)	220 - 340	15~20	Heating Gasoil Fuel Oil
Heavy Cycle Oil (HCO)	340 - 450	5~15	Recycling Thermal Cracking
Residue/Slurry	450+	5~10	Thermal Cracking
Coke		3~5	Burnt in regenerator

- Its price evaluation is determined by refinery optimization team to be based on Prem. Unleaded 10ppm international prices with a small premium added on top. The same applies to isomerate, reformate and alkylate streams, with different premia added on top, depending on the value of each stream. Optimization staff evaluates the corresponding premia in line with the presence of these streams in the blended material. The more the percentage a stream gets blended the more its value for producing the final product. The above generic rule does apply to alkylate, if alkylate is not produced through alkylation process within the boundaries of the refinery. In that case the Supply and Trading Division (S&T) will advise on the cost of alkylate import. Another way to determine the value of naphtha, isomerate and reformate is to get feedback from S&T after intermediates/feedstock international market investigation.

- Isomerate is the product of isomerization, a process which is described in detail herebelow.
- LSR stands for Light Straight Run Naphtha and comes directly from distillation unit. After undergoing a pretreatment with hydrogen (see graph below) LSR feeds the isomerization unit. Not the entire available quantity reacts to produce isomerate, therefore the remaining is stored and is used for blending purposes, feeding directly the gasoline blender.
- Reformate is the product of reformer unit, shortly called CCR (Continuous Catalytic Reformer). This unit is described in extend below.
- TRN is characterized a kind of heavy naphtha (distillates at 80-160°C) that is hydrotreated first and feeds the reformer to produce reformate. Similar to isomerization process, not whole TRN quantity which is available in the refinery is converted, therefore the surplus is stored and is used as gasoline blending component.
- Mtbe/Etbe and Alkylate are chemical compounds that are analyzed below.

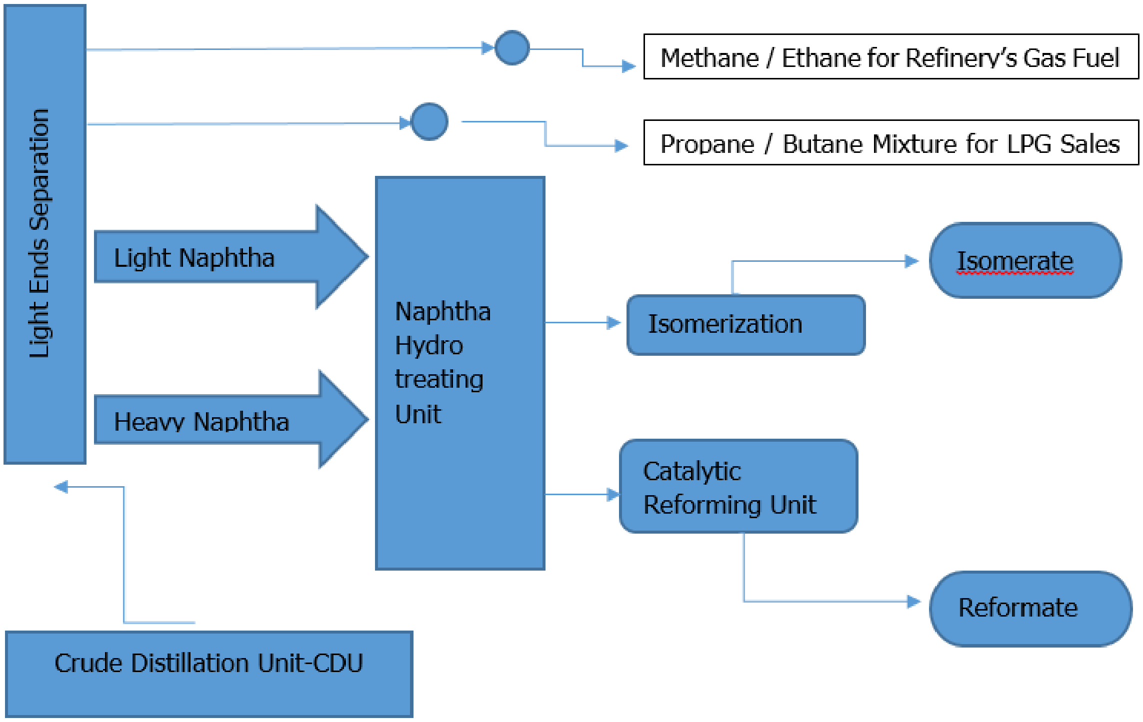


Figure 5 Light Ends Refining Process Flow

It's time to analyze the input streams of gasoline blender. Let's examine how they are produced in the refinery sequence scheme, what are their characteristics and the main parts and operating conditions of the units they are produced from.

FCC Naphtha

Oil refinery industry discovered that hydrocarbons with higher boiling points (the larger ones distilled in the bottom of the distillation column) could be broken down (cracked) into lower-boiling hydrocarbons by exposed to very high temperatures. This process, commonly known as "thermal cracking" was widely used to increase gasoline production back in 1913 and gradually was supplemented by a catalyst, to be evolved into "catalytic cracking". The catalyst speeds up and facilitates the chemical reaction without undergoing a permanent chemical change itself. Catalytic cracking produces gasoline of higher quality than thermal cracking. There are many variations on catalytic cracking, but fluidized catalytic cracking (FCC) is the heart of gasoline production in most modern refineries. The term comes from the practice of fluidizing a solid catalyst so that it can be continuously cycled from the reaction section of a cracker to the catalyst regeneration section and back again.

The typical feedstock in an FCC Unit is the gasoil and more precisely various refining streams with the boiling range between 317°C and 575°C, including but not limited to atmospheric gas oils, vacuum gas oils, coker gas oils. Various contaminants, such as sulphur, nitrogen and metals are present in gasoil feed. To protect the catalyst, pre-treatment by hydrotreating is required in order to remove contaminants and improve cracking characteristics and yields. Gas oil from residue and conversion processes (predominantly coking) can be fed to catalytic cracking units. They must be hydrotreated before catalytic cracking to separate aromatics and remove sulphur. The principal limitation on charge stocks are the Conradson Carbon Residue (CCR) and metal contaminants. The effect of Conradson carbon is to form a deposit on the catalyst. This deposit could be beyond the burning capacity in the regenerator. For atmospheric residue, it is desulphurised first in the Atmospheric Residue Desulphurization (ARD) reactor units. Vacuum residue must also desulphurised and may be deasphalted before used in the FCC. Special Residue FCCs are designed to handle such heavy feeds.

The process flow diagram is presented below. The vacuum gasoil (VGO) feed is heated up to 315-425°C and is mixed with the hot regenerated catalyst (640-760°C) at the bottom of the riser, which is a long vertical pipe. The liquid feed is vaporized due to the hot catalyst and goes up in the riser for a short period of time, normally 2-10 seconds. The temperature at the riser outlet is the key factor in determining the conversion and product quality. At riser's top the temperature could reach the 550^{o}C. The riser is the main reactor in which the endothermic reactions take place. High temperature favors olefin-rich light gases production, moderate temperature favors gasoline production and lower temperature increases the distillate yields.

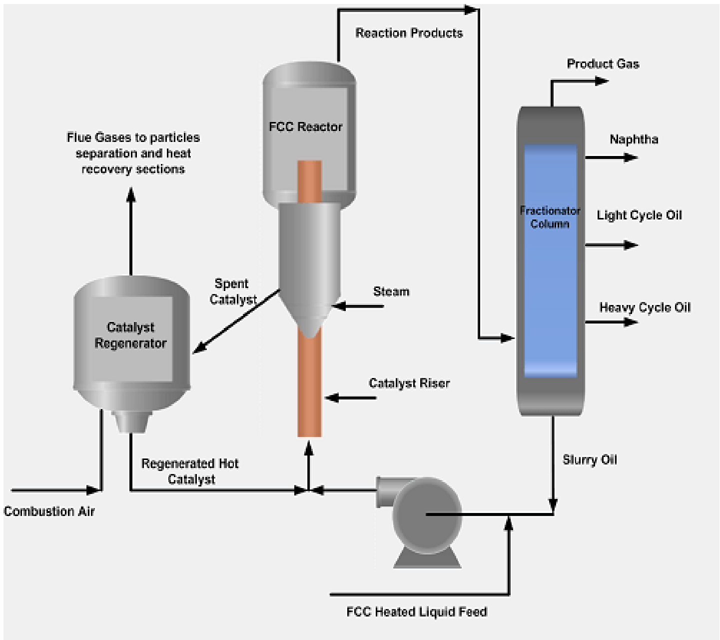


Figure 6 Fluid Catalytic Cracking - Main Parts

The gaseous products exit from the top of the riser and flow straight into the fractionator column. At the same time the separated catalyst and some heavy liquid hydrocarbons flow back into the disengagement section of FCC reactor. Steam is also injected into the stripper to remove the oil from the spent catalyst. The oil is stripped and moves along with the rising vapors to the fractionator. The used catalyst is sent to the regenerator at a temperature of 475-550^{o}C.

The coke on the spent catalyst is burnt off in the regenerator by introducing air. Excess air is utilized to ensure the efficient combustion of coke. The produced flue gases, containing carbon monoxide, carbon dioxide, water and excess air, can be sent to power recovery unit to produce superheated steam.

The FCC unit achieves a steady state and remains in that state as long as a heat balance exists between the heat produced in the regenerator and the heat consumed in the reactor. In both pieces of equipment hydro cyclones are installed to remove any solid catalyst carried in the overheated gaseous stream.

There are three types of commercial FCC cracking catalysts, 1. acid-treated natural aluminosilicates, 2. amorphous synthetic silica-alumina combinations, and 3. crystalline synthetic silica-alumina catalysts called zeolites or molecular. Zeolite types catalysts are preferred over other types due to higher activity, higher gasoline yields, production of gasoline containing a larger percentage of paraffinic and aromatic hydrocarbons, lower coke yield, increased isobutane production, and ability to go to higher conversion, high hydrogen transfer, hence saturation of products takes place at the primary steps of cracking.

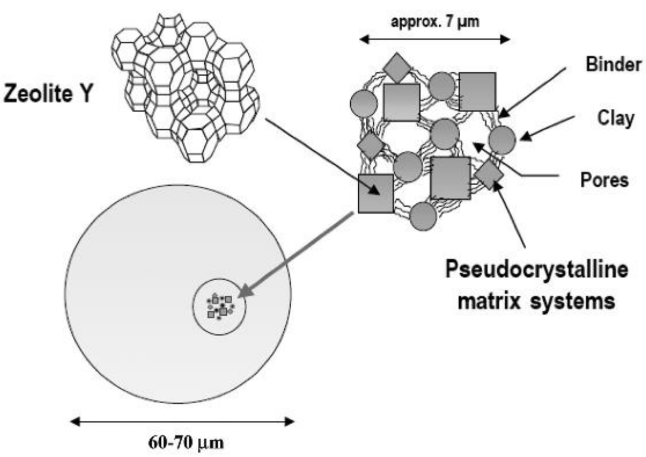


Figure 7 FCC catalyst magnified

One of the significant developments in FCC practice was the introduction of zeolite catalysts in 1965. Catalysts and additives play a major role in the selectivity and flexibility of FCC processes. FCC catalyst consists of a fine powder with an average particle size of 60–75 µm and a size distribution ranging from 20 to 120 µm. Four major components make up the catalysts: zeolite, active matrix, filler, and binder. Each of these constituents has a unique role to play, but zeolite is the key component that is more active and selective for high-octane number gasoline production

ISOMERATE

Isomerate is the product of Isomerization Unit. Isomerization increases octane number of gasoline pool by converting straight-chain (typically mixture of C5 and C6) paraffins into their branched isomers. An isomer is a molecule or compound that has the same number of atoms as another but different arrangement, which produces different physical and chemical properties. The feed of the unit is light naphtha (mixture of C5 and C6) which has been hydrotreated to capture nitrogen, sulphur and water. In the equilibrium the products comprise from small quantities of gases, produced from cracking, unconverted paraffins and iso-paraffins along with naphthenes.

We can distinguish between:

- Once-Pass Isomerization Process which is a fixed-bed process with catalyst of acidic zeolite reinforced with a noble metal. Process temperature is 245-270°C and pressure 21-

35 kg/cm^2 with the presence of hydrogen. The typical reaction efficiency is 97-98% of the liquefied feed and the Octane Number increase is about 10-12 units, resulting in isomerate product with RON 77-80.

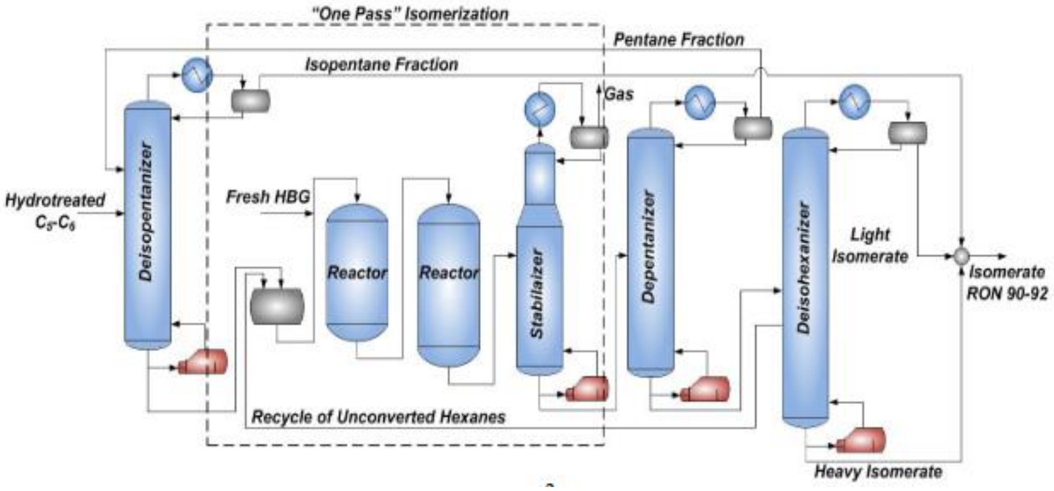


Figure 8 Once-Pass Isomerization Process

- Total Isomerization Process, TIP combines the above one-through isomerization using zeolithic base catalyst with the process of IsoSiv for detailed naphthenes separation. The final product presents Octane Number (RON) 87-90, a total increase of about 20 units compared to the light naphtha feed. The n-paraffines which didn't react in the first stage, are absorbed in the molecular sieves and are recycled back to the main reactors to be converted with hydrogen usage. Hydrogen presence in this stage prevents "coke" blocking of the sieves. The whole process opts for steady, low pressure.

  There are some undesired H/C in the feed of the process. In terms of olefins the catalyst of the process cannot handle more than 2% C5/C6 olefins because they tend to polymerize on the surface of the catalyst. As a result we cannot feed FCC naphtha or naphtha originated from a visbreaker or coker unit.

  In addition naphthenes and aromatics, if they are present in the feed of the unit, they are absorbed in the reaction centers of the catalyst and reduce catalyst's effectiveness in the isomerization of paraffins process. In case that feed contains significant amount of aromatics, like benzene, we need to increase the catalyst volume in the reactor. The unsaturated aromatics consume significant amount of hydrogen, due to the exothermic hydrotreating reactions. This effect does not ease the desired equilibrium of isomerization reactions. Benzene is hydrotreated rapidly and transformed into cyclo-hexane and in sequence the cyclo-hexane and the other C6 naphthenes are partially transformed into C6 paraffines. The C7 hydrocarbons are pyrolyzed into C3 and C4 and those molecules that are not converted, they effectively undergo isomerization process with higher octane number than the normal (n-) isomers C5 or C6. The C7 naphthenes have similar behavior with C6 naphthenes.

One TIP Isomerization Unit can be broken down to three stages:

- The conversion stage, which includes the reactors and the section of methanol preparation for reacting with hydrocarbons
- The stage of absorption and release of the paraffins that didn't react from the molecular sieves.
- The separation stage of the final product (isomerate) from the lighter sub-products (pyrolyzed hydrocarbons).

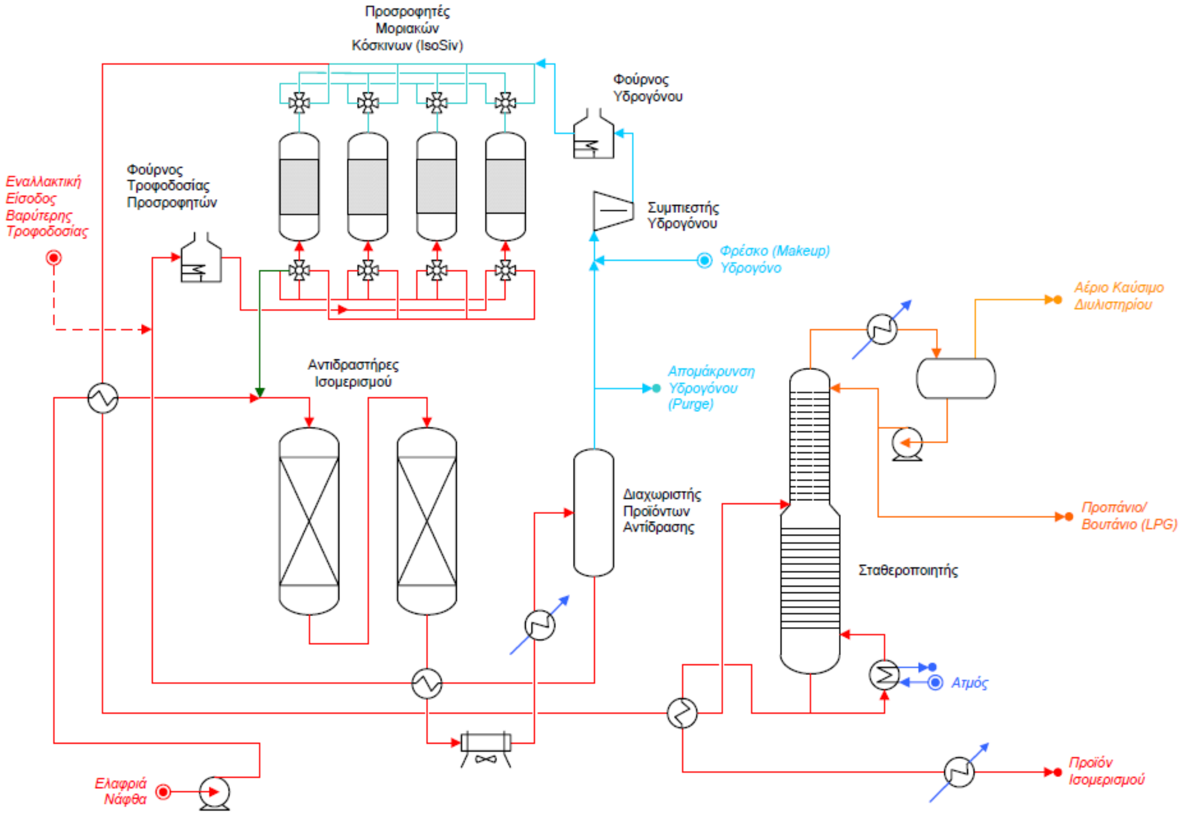


Figure 9 TIP Isomerization Process

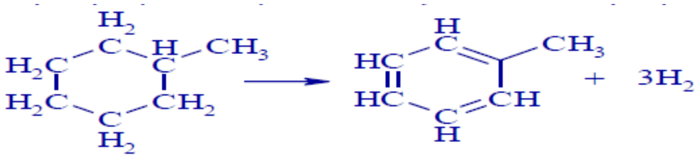
REFORMATE

Reformate is the product of the process called Catalytic Reforming. The heavy naphtha as side product of Atmospheric Distillation Unit has a really low octane number and it cannot be used for gasoline production. This is why the process of catalytic reforming is used. During this process the naphthenes are dehydrogenated and paraffins are converted to aromatics with higher octane number and hydrogen, with a presence of catalyst. Hydrogen is a precious substance for the refinery processes, which is widely used in the hydro-treatment units. The feed is heavy naphtha at temperature of 80-160oC which has already undergone a hydro-treatment to capture hetero-atoms, like sulphur, nitrogen and water.

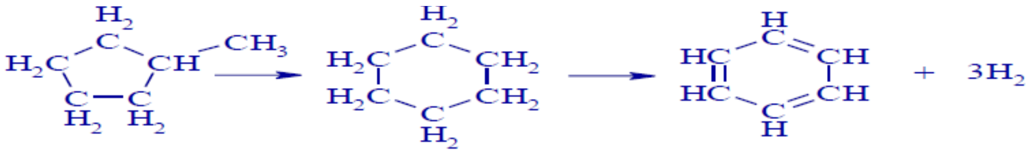
The process applies to naphtha streams with limited content in sulphur. Reforming cannot treat catalytic pyrolized naphtha product due to high concentration in olefins and aromatics. Pyrolized naphtha is commonly treated through alkylation process for Alkylate production; another important gasoline blending component, with really high octane number. Likewise, reforming cannot treat thermal pyrolized naphtha due to high concentration in sulphur, olefins and aromatics. The catalyst is Pt on top of alumina, typically the most expensive catalyst in a modern refinery. Sulphur is the major inhibitor of the catalyst, this is why – as already mentioned – the feed is hydro-treated beforehand.

The following chemical reactions principally take place during the catalytic reforming process:

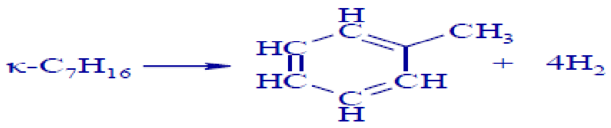
Dehydrogenation of cyclo-hexane for formation of aromatics:



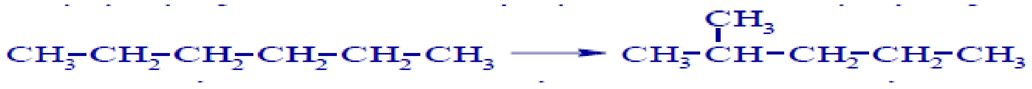
Dehydrogenation and isomerization of alky-pentane:



Dehydrogenation of n-paraffins resulting in aromatics formation:

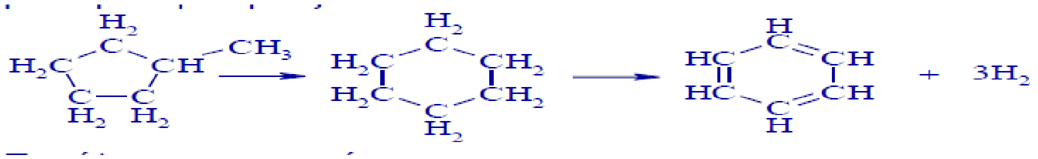


Isomerization of n-paraffines to iso-paraffins:

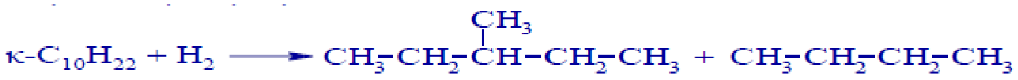


$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_2-CH_3$$

Isomerization of alkylo-pentanes into cyclo-hexane and subsequent transformation into benzene:



Paraffins pyrolysis:



$$\kappa\text{-}C_{10}H_{22} + H_2 \longrightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_3 + CH_3-CH_2-CH_2-CH_3$$

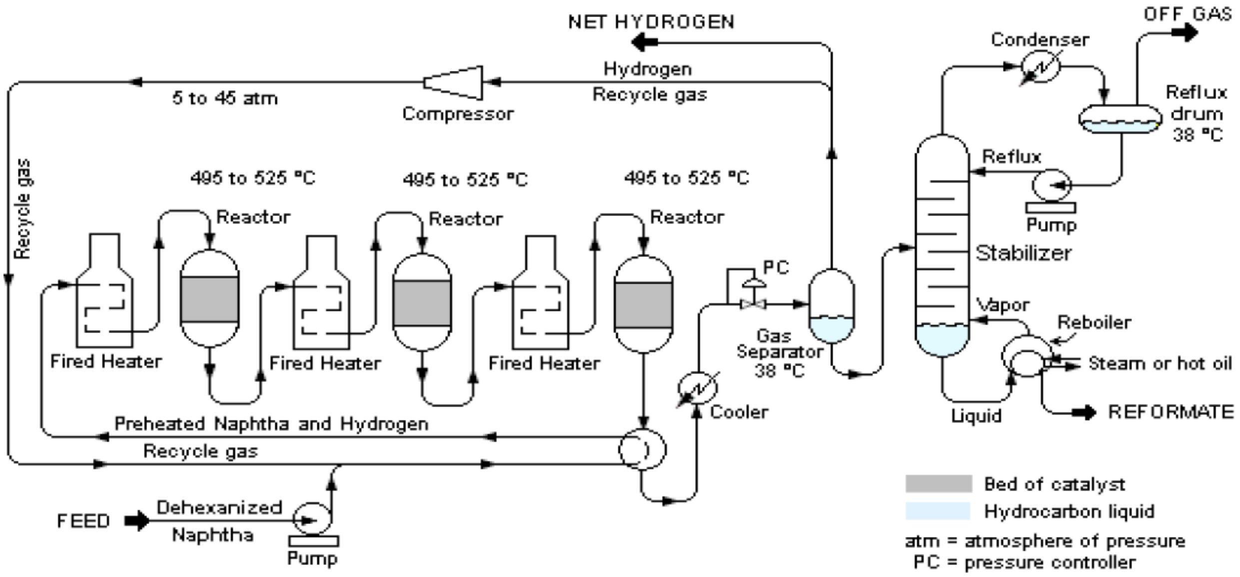


Figure 10 Reformer Unit

MTBE

The constantly increasing concerns about fossil fuels sustainability, coupled with the changes in legislation aiming to reduce greenhouse gas emissions, have forced industry to search for renewable fuels with lower carbon footprint to replace (partially or entirely) the conventional fuels. Oxygenate additives contain oxygen as part of their chemical structure and are largely used as gasoline additives. They increment the octane number and combustion quality of gasoline and reduce particulate emission and carbon monoxide production.

Methyl tert-butyl ether (MTBE) is a common chemical used as an octane booster agent as a substitution to tetra ethyl lead. It is produced with reaction of iso-butylene with methanol, as per following flow diagram.

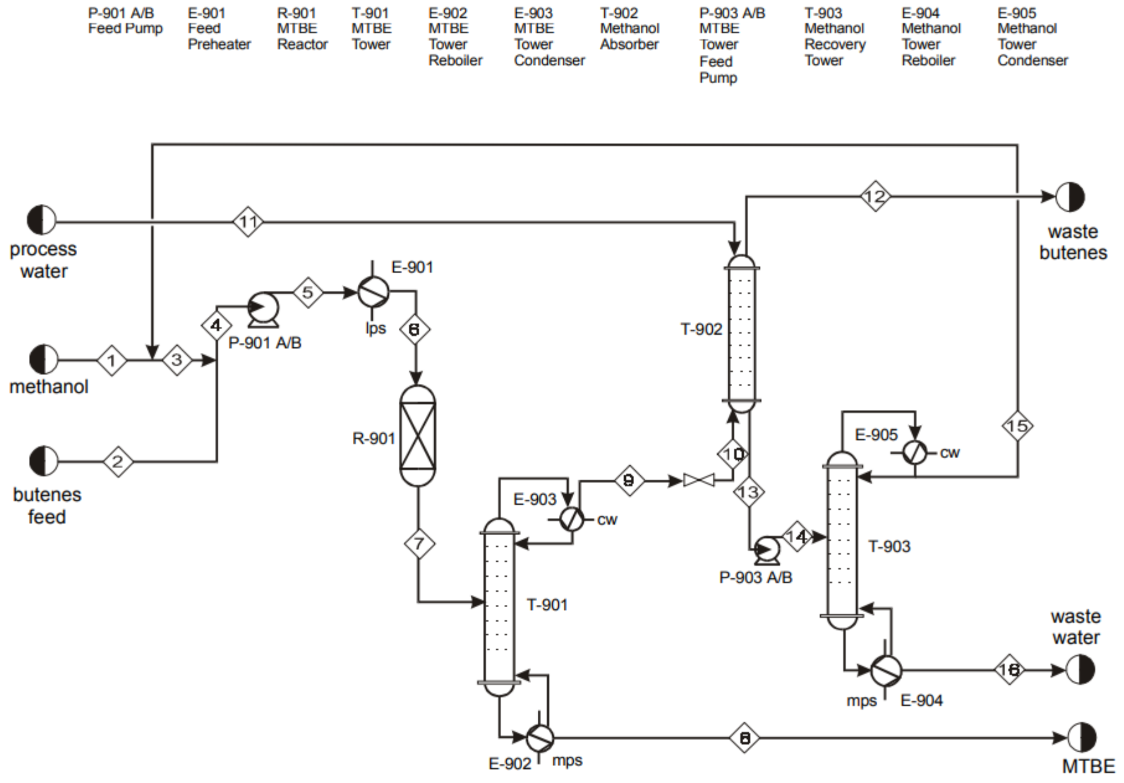
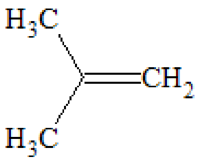
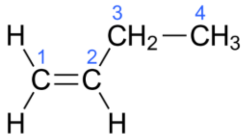
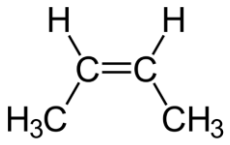


Figure 11 MTBE production flow diagram

Methanol is usually purchased from a refinery operator and iso-butylene is obtained from the refinery processing system. The latter stream contains a mix of:

iso-butene	**1-butene**	**2-butene**
		

There are five basic reactions that occur in the production of MTBE from crude vacuum residue. The first step is the partial oxidation of the carbon and hydrogen in the vacuum residue stream using pure oxygen:

$CnHm\ (l) + n/2\ O2\ (g) \rightarrow n\ CO\ (g) + m/2\ H2\ (g)$ (1)

The next reaction is the water gas shift reaction, which is used to adjust the H2 to CO ratio for the optimal production of methanol:

$CO\ (g) + H2O\ (g) \rightarrow CO2\ (g) + H2\ (g)$ (2)

Methanol is then produced from carbon monoxide and hydrogen by the reaction:

$CO\ (g) + 2\ H2\ (g) \rightarrow CH3OH\ (g)$ (3)

The formation of dimethyl ether and water from carbon monoxide and hydrogen also occurs as a side reaction when producing methanol:

$2\ CO\ (g) + 4\ H2\ (g) \rightarrow C2H6O\ (g) + H2O\ (g)$ (4)

The final reaction involves the production of MTBE from methanol and isobutylene:

$CH3OH\ (l) + C4H8\ (l) \rightarrow C5H12O\ (l)$ (5)

E.T.B.E.

Ethyl tert-butyl ether is a widely used as an oxygenate additive to gasoline. The main drawback of ETBE manufacture is the energy intensive product recovery process, making its production quite expensive. The purification process of ETBE involves the separation of ETBE, mixed C4 hydrocarbons and unreacted ethanol. The unreacted ethanol forms azeotropic mixture with ETBE, which is difficult to be separated through distillation. For improving this separation the use of a hybrid distillation-pervaporation process with alcohol-selective membranes, which allows to reach the target of ETBE purity of 95.2% with a lower energy consumption. At the same time the permeate stream, with a high ethanol content, is recycled back to the reaction. Alternatively, the production of ETBE by means of reactive distillation allows a significant increase in the conversion of the reactants, but in contrast, the energy consumption is higher than the other processes mentioned.

In principal ETBE production follows the above process of MTBE production with slight modifications but the main difference is the use of ethanol as feedstock instead of methanol. Ethanol is primarily imported to refinery system and for European refining industry is quite expensive, because it's imported from USA or Latin America.

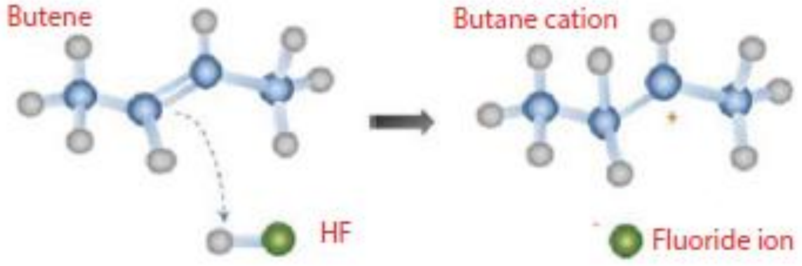
ALKYLATE

Alkylate is an excellent blending component for gasoline. It's composed of a mixture of high-octane, branched-chain paraffinic hydrocarbons (mostly iso-heptnane and iso-octane), having a high octane number, due to its high content of branched paraffins. At the same time, alkylate is free of aromatics and olefins and it has a low Reid Vapor Pressure (RVP). Using alkylate in the blending recipe, the possibility of butane to be used is reduced. The process employs isobutene (iC_4) and low molecular weight alkenes, primarily a mixture of propylene (C_2H_6) and butylene (C_4H_8) into alkylate, a branched-chain paraffinic fuel. The product yield is maximized in the presence of a strong-acting acid, such as sulfuric acid (H_2SO_4) and hydrofluoric acid (HF) as catalyst. Depending on the catalyst that is used the process is named either Sulfuric Acid Alkylation Unit (SAAU) or Hydrofluoric Acid Alkylation Unit (HFAU). The technologies for sulfuric acid and hydrofluoric acid have each held 50% of the market share for alkylation. However in late 1980s, several hydrofluoric acid (HF) releases as well as industry testing showed that HF acid forms a relatively long-lasting aerosol when released into the atmosphere, with large potential to form a toxic cloud that could extend beyond the boundary of the refinery. These events resulted in the evaluation of the merits of both hydrofluoric acid alkylation unit (HFAU) and sulfuric acid alkylation unit (SAAU) technologies and resulted in the removal of HF alkylation making sulfuric acid as the catalyst of choice.

The reaction of alkylation involves the following steps:

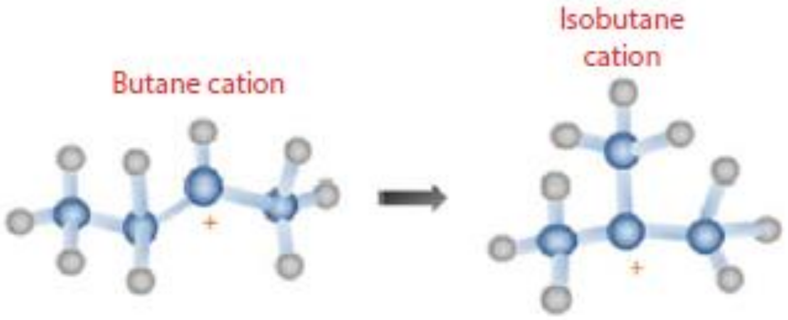
Step 1: Cation formation

In the HF alkylation unit, the olefin molecule reacts with the HF acid catalyst. The olefin double bond attracts the hydrogen atom from the HF acid molecule. In that way olefin molecule becomes a cation (positively charged), as it bonds to hydrogen and fluoride ion is formed at the same time.



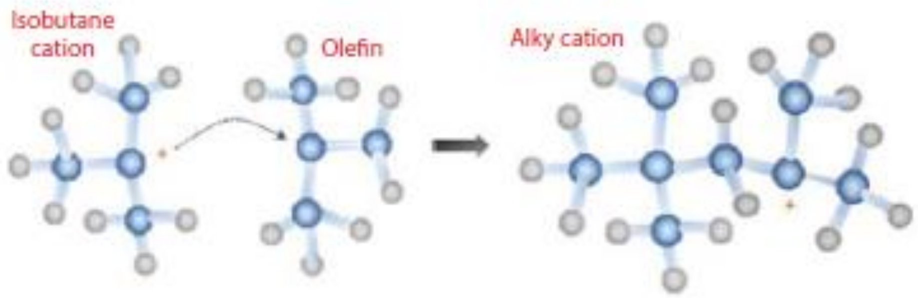
Step 2: Cation Rearrangement

Before combining with an olefin the butane cation rearranges itself to form an isobutene cation.



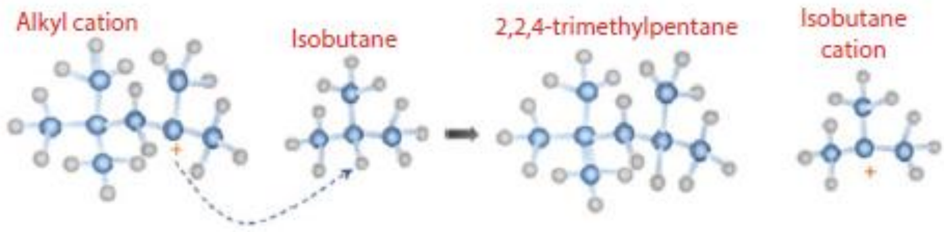
Step 3: Pairing

The isobutene cation then reacts with another olefin molecule to create a larger cation.



Step 4: Chain Termination

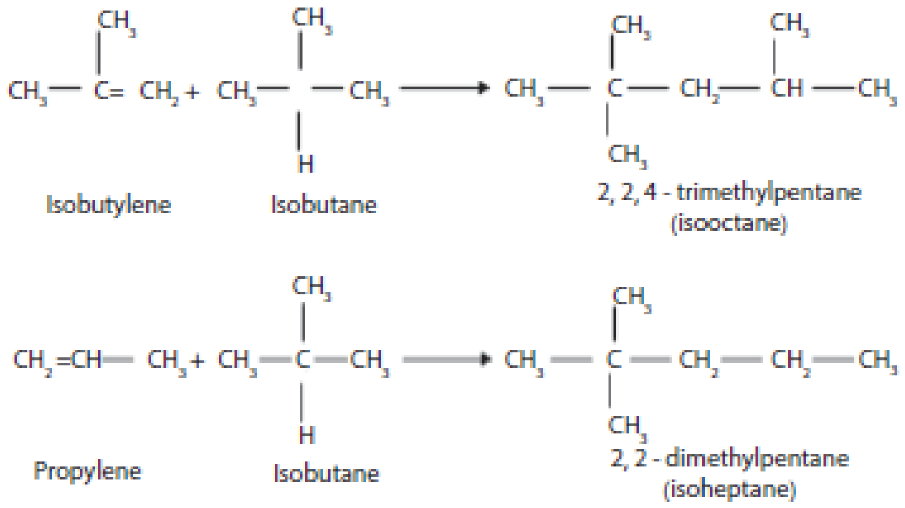
Isobutane which is essential in the process, transfers on hydrogen atom to Alky cation of previous step very readily. This occurs because the isobutene has tertiary hydrogen, thus driving the importance of monitoring the alkyl isobutene / olefin ratio. In this step a formation of isobutene cation is formed, propagating the next reaction.



Step 5: Catalyst recovery

Since the role of HF is to act as catalyst, the fluoride ions recombine with the hydrogen ions to form a HF molecule.

The principal reactions that occur in alkylation are the combination of olefins with isoparaffins, as follows:



FINAL PRODUCTS – QUALITY ATTRIBUTES DEFINITION

REID VAPOUR PRESSURE – RVP

This attribute of a gasoline blend affects the gasoline performance in terms of ease of starting, engine warm-up, and rate of acceleration. RVP is the vapour pressure at 100 °F of a product determined in a volume of air four times the liquid volume. RVP is not an additive property. Therefore, in this case we need to use a blending index. A commonly used index has been introduced by Chevron Oil Trading Company (1971) as per below:

$$BI_{RVP(i)} = RVP(i)^{1.25}$$

where $BI_{RVP(i)}$ is the RVP blending index for component i and RVP(i) is the RVP of component i in psi.

Using this index, the RVP of the blend is estimated as:

$$BI_{RVP,blend} = \sum_{i=1}^{n} x(vi)BI(RVPi)$$

Where x_{vi} is the volume fraction of component i.

OCTANE NUMBER

Many alternative methods have been proposed for estimating the octane number of gasoline blends since the simple mixing rule needs minor corrections. One correction method that uses the octane number index has been reported by Riazi (2005). The following octane index correlations depend on the octane number range as follows:

For $11 \leq ON \leq 76$

$BI_{Oni} = 36.01 + 38.33*(ON/100) – 99.8*(ON/100)^2 + 341.3*(ON/100)^3 – 507.02*(ON/100)^4 + 268.64*(ON/100)^5$

For $76 \leq ON \leq 103$

$BI_{Oni} = -299.5 + 1272*(ON/100) – 1552.9*(ON/100)^2 + 651*(ON/100)^3$

For $103 \leq ON \leq 106$

$BI_{Oni} = 2206.3 – 4313.64*(ON/100) + 2178.57*(ON/100)^2$

The octane number index for a blend can be determined using the following equation:

$BI_{ON,\ blend} = \sum_{i=1}^{n} x(vi)BI(ONi)$

where x_{vi} is the volume fraction of component I and $BI_{ON(i)}$ is the octane number index of component I that can be calculated by the above equations.

RON BONUS / MON BONUS TECHNIQUE

Another way to determine the Octane Number of the blended material is by evaluating extended experimental data of the final product after mixing. For example the Optimization dept. of a Mediterranean located refinery has conducted the following table for RON/MON attributes of each of the blending streams:

Table 5 RON/MON Bonus Technique

	FCC naphtha	**Reformate**	**LSR**	**TRN**	**C4**	**ETBE**	**MTBE**	**Isomerate**	**Alkylate**	**BLEND properties**
ACTUAL RON	**92,0**	**103,1**	**69,4**	**48,0**	**101,0**	**113,7**	**114,6**	**86,0**	**92,8**	
ACTUAL MON	**81,0**	**92,2**	**65,4**	**45,0**	**88,1**	**102,1**	**102,8**	**84,0**	**91,6**	
Δ (RON-MON)	11,0	10,9	4,0	3,0	12,9	11,6	11,8	2,0	1,2	
RON Bonus	0,0	1,0	6,0	10,0		2,0	0,0	1,0	2,0	
MON Bonus	-1,4	-1,0	4,0	10,0	0,0	-3,5	-6,5	0,0	0,1	
RON prediction	92,0	104,1	75,4	58,0	101,0	115,7	114,6	87,0	94,8	**95,6**
MON prediction	79,6	91,2	69,4	55,0	88,1	98,6	96,3	84,0	91,7	**85,0**

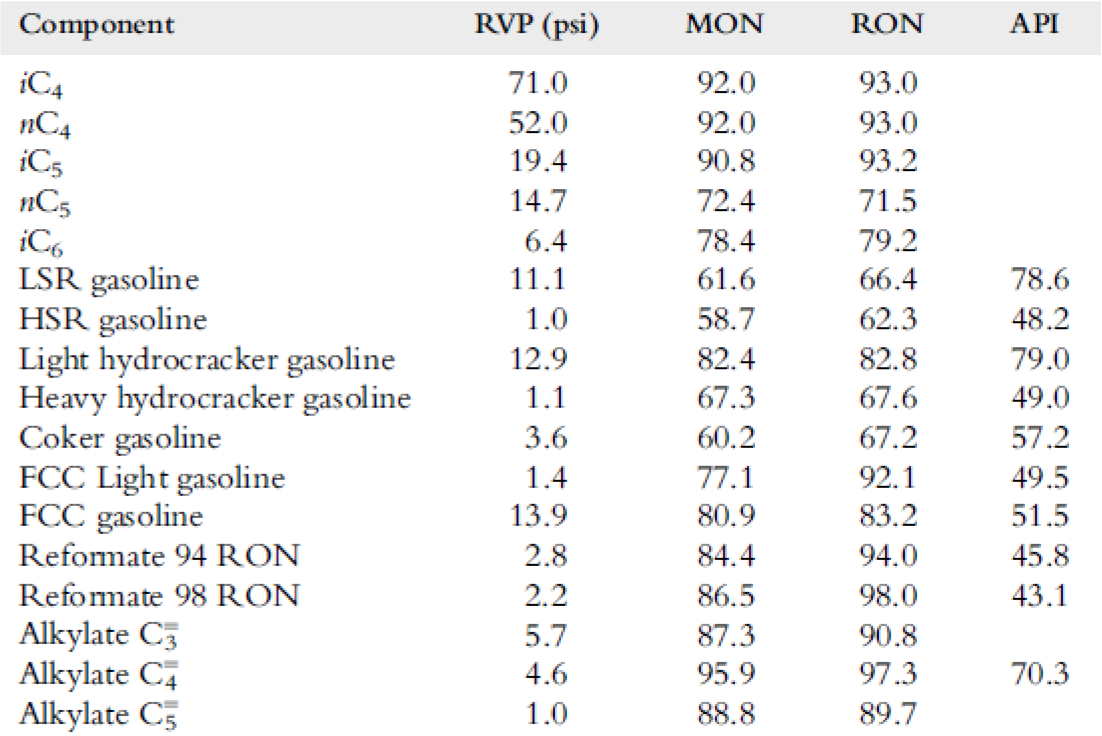
The "Actual RON" and "Actual MON" entries are the values measured by refinery's chemistry lab for each stream. In addition the RON/MON data of final products, as the outcome of many different blending processing events, are collected and assessed frequently. Refinery's personnel is always aware of the proportion of each components in the final product, therefore can readily assign a value (it can be positive or negative), a kind of bonus to the measured value according to their effect (non-linear) at the RON/MON attribute of gasoline. The positive figure addresses the higher contribution of this stream than expected basis on its typical/measured value in the final product and the negative figure corresponds to the opposite outcome. The sum of "Actual" figure and "Bonus" figure result in "RON Prediction"/"MON Prediction" values, which consequently are treated like-having linear behavior in blending operation. In this way the last column in the above table "Blend Properties" is conducted, in terms of this specific quality requirement.

The attributes of every blending stream vary according to deferent factors:

1. The crude slate that every refinery has access to, depending on geographical limitations, political agreement between governments or other limitation (sanctions, war risk etc) beyond the control of the refinery company. All crude oils are not the same. The have different netback on the products, different sulphur content and different density.
2. The conditions ever refinery picks to run, according to its units, set-up of the units, production capacity, storage capacities, product variance demand
3. The specs that intermediate (not ready products) materials the refinery can source, depending on the geographical position and the economics related to logistics of supply.

Due to the above reasons, the typical properties for gasoline blending components, in a typical US refinery scheme, according to Gary and Handwerk, 2001 have the following profile:

Table 6 Typical properties of gasoline components according to Gary and Handwerk



Component	RVP (psi)	MON	RON	API
iC_4	71.0	92.0	93.0	
nC_4	52.0	92.0	93.0	
iC_5	19.4	90.8	93.2	
nC_5	14.7	72.4	71.5	
iC_6	6.4	78.4	79.2	
LSR gasoline	11.1	61.6	66.4	78.6
HSR gasoline	1.0	58.7	62.3	48.2
Light hydrocracker gasoline	12.9	82.4	82.8	79.0
Heavy hydrocracker gasoline	1.1	67.3	67.6	49.0
Coker gasoline	3.6	60.2	67.2	57.2
FCC Light gasoline	1.4	77.1	92.1	49.5
FCC gasoline	13.9	80.9	83.2	51.5
Reformate 94 RON	2.8	84.4	94.0	45.8
Reformate 98 RON	2.2	86.5	98.0	43.1
Alkylate $C_3^=$	5.7	87.3	90.8	
Alkylate $C_4^=$	4.6	95.9	97.3	70.3
Alkylate $C_5^=$	1.0	88.8	89.7	

Respectively, the chemical attributes of gasoline blending components in a Mediterranean Refinery, appear to be similar to the following:

Table 7 Typical properties for gasoline blending components in a Complex Med-based Refinery

	FCC naphtha	**Reformate**	**LSR**	**TRN**	**C4**	**ETBE**	**MTBE**	**Isomerate**	**Alkylate**
RVP, kpa	64,12	40,0	78,6	6,9	411,6	35,8	55,2	86,2	40,0
R.V.P.,psiA	9,3	5,8	11,4	1,0	59,7	5,2	8,0	12,5	5,8
RVPIndex	144,8	83,9	183,3	11,0	1242,6	74,0	121,7	203,9	83,9
RVPtot, psi									
RVPtot, Kpa									
Vapour Lock Index									
FBP	176,5	204,0	97,1	163,9	3,0	140,0	85,0	159,0	202,0
Evaporated @70 C, vol%	25,0	5,0	91,0	0,0	100,0	4,0	96,0	74,0	5,0
Evaporated @100 C, vol%	52,7	17,0	100,0	0,0	100,0	80,0	100,0	93,4	47,6
Evaporated @150 C, vol%	82,0	74,0	100,0	0,0	100,0	90,0	100,0	100,0	93,0
ACTUAL RON	**92,0**	**103,1**	**69,4**	**48,0**	**101,0**	**113,7**	**114,6**	**86,0**	**92,8**
ACTUAL MON	**81,0**	**92,2**	**65,4**	**45,0**	**88,1**	**102,1**	**102,8**	**84,0**	**91,6**
Δ (RON-MON)	11,0	10,9	4,0	3,0	12,9	11,6	11,8	2,0	1,2
RON Bonus	0,0	1,0	6,0	10,0		2,0	0,0	1,0	2,0
MON Bonus	-1,4	-1,0	4,0	10,0	0,0	-3,5	-6,5	0,0	0,1
RON prediction	92,0	104,1	75,4	58,0	101,0	115,7	114,6	87,0	94,8
MON prediction	79,6	91,2	69,4	55,0	88,1	98,6	96,3	84,0	91,7
Sulfur (%wt.)	18,5	0,0	0,2	0,2	0,0	8,8	3,3	0,0	1,3
Aromatics (%vol)	13,8	72,5	1,6	9,0	0,0	0,0	0,0	5,0	0,7
Ethers (%vol)	2,4					91,0	95,8		0,0
Density (g/ml)	0,717	0,817	0,669	0,750	0,588	0,743	0,746	0,669	0,700
Benzene (%vol)	1,1	1,4	1,4	0,7	0,0	0,0	0,0	0,2	0,0
O2 (%wt)	0,4	0,0	0,0	0,0	0,0	14,9	17,4	0,0	0,0
Bio-ethers (%vol)	2,4	0,0	0,0	0,0	0,0	91,0	0,0	0,0	0,0
Olefins (%vol)	35,2	0,0	0,0	0,0	57,0	3,0	0,0	0,0	0,0

LINEAR PROGRAMMING, THE APPROACH

Mathematical programming is “programming” in the sense of “planning”, thus is completely different from computer programming. As such it has nothing to do with computers. Inevitably mathematical programming becomes involved with computing, since practical problems always involve large amount of data and arithmetic which can reasonably be tackled by the calculating power of a computer. The common feature which mathematical models have, is that they involve optimization. We wish to maximize or minimize something. The quantity which we want to maximize or minimize is known as an objective function.

First we need to decompose the blending problem to the below four partial problems.

1. Optimization of Unleaded 95Ron production for domestic market
2. Optimization of Unleaded 98Ron production for domestic market
3. Optimization of Unleaded 100Ron production for domestic market
4. Optimization of Unleaded 95Ron production for exports

In the last case the Mediterranean located refinery exports the excess gasoline production capacity to increase its revenue, even if its selling price is considerably lower than the prevailing prices of domestic market.

We need to declare the **independent variables** first. Those shall be the quantities in metric tons of each of the blending component for producing each final product. Subsequently, the **dependent variables** of the problem will be the quantities in metric tons of the above final products. These variables are dependent to blending streams in the sense that due to mass balance of the blender, for each bending mode i.e. production of each product, the mass of every stream that compose the product shall be accumulated to the total mass of the produced commodity. Therefore we can write down the below mass balance equations referring to optimization problems 1 through 4 respectively.

x1dom95 + x2dom95 + … + x9dom95 = ydom95

x1dom98 + x2dom98 + … + x9dom98 = ydom98

x1dom100 + x2dom100 + … + x9dom100 = ydom100

x1exp95 + x2exp95 + … + x9exp95 = yexp95

The optimization problems 1 and 4 are quite similar. The only difference applies in the quality requirements of the final product (domestic vs export market oriented). Those requirements are represented in the optimization algorithm through the quality constraints that we will review here below.

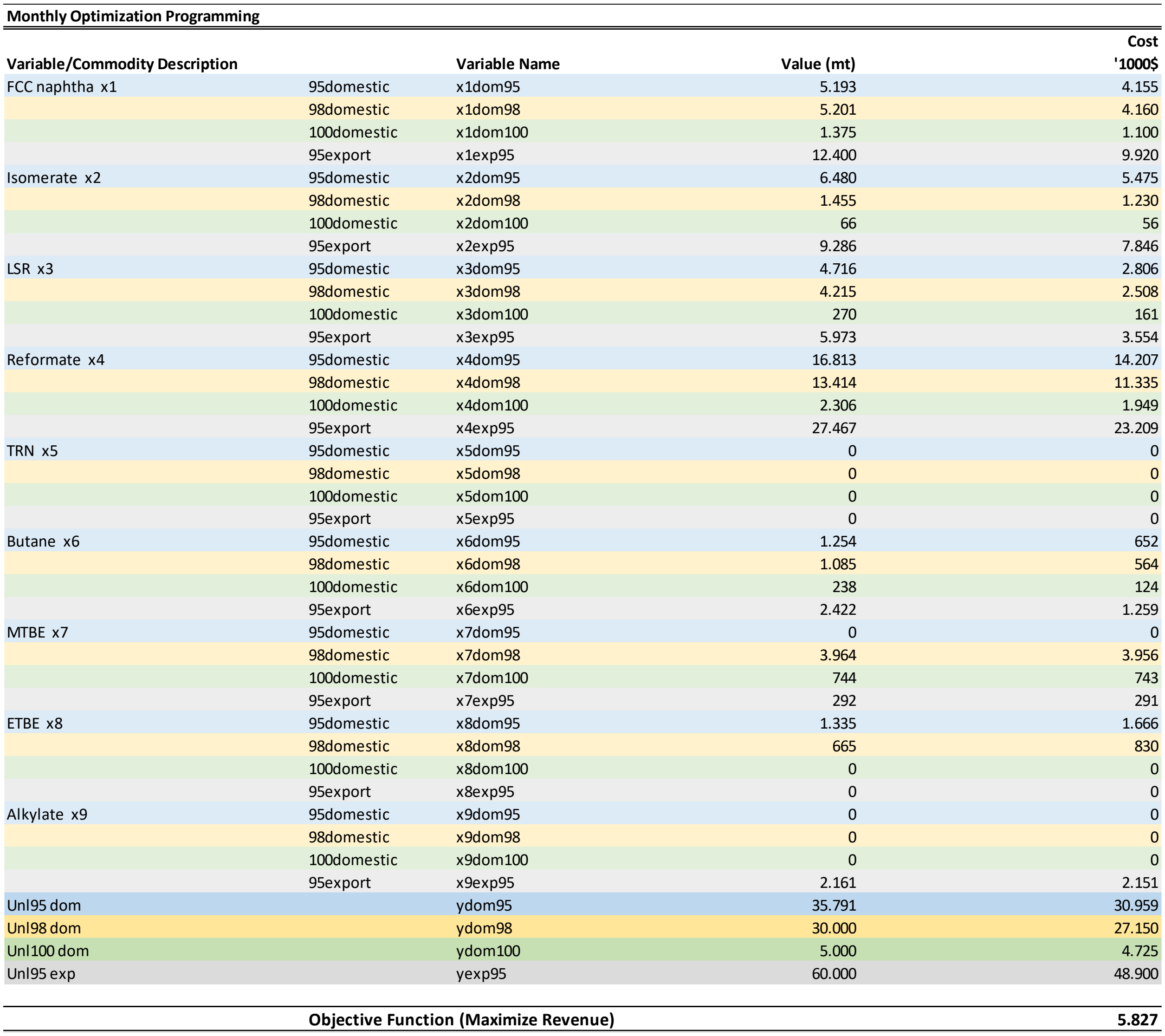
In the first problem, the objective function is to maximize revenue after selling the final product "Unleaded 95Ron for domestic market" on a monthly basis. Let's call that variable "ydom95". We have given initial values for the linear programming subroutine of Excel ("Solver") to start iterating the values of variables and calculate the value of objective function. The same procedure is followed for the rest of the isolated problems in order to realize the limitations and drawbacks of our analysis.

After analyzing each of the above separate problems, we'll optimize the entire gasoline production scheme of the refinery for one particular month (winter month – has to do with gasoline specs straight related to quality constraints).

The working steps are the following:

- We need to define the variables of the entire problem. As discussed before they should be the quantities (in metric tons) of the blending stream in the blending process of each of the final products. These are all independent variables. Also we declare the dependent variables of the metric tons of the final products themselves. The following table summarizes the whole set of our variables.
- We also need to clearly define the objective function of the optimization problem. It often seems that real-world problems are most naturally formulated as minimizations (since real-world planners always seem to be pessimists), but when discussing mathematics it is usually nicer to work with maximization problems. In our case, the objective function, which literally illustrate our ultimate goal, must be either to minimize cost of producing the monthly requested products or maximizing the revenue produced out of selling these products. We decide to go with the latter objective function as presented in the below table.
- As discussed, every variable has a price. Therefore, in the column "Value" the quantity of the variable is quoted and in the column "Cost" the respective cost in thousands of $ is quoted. The sum of the "Cost" values of products minus the sum of the "Cost" values of blending components produce the final value of our objective function.
- We need to underline that prices are changing every single trading/working day. Therefore the respective "Cost" values are changing every day. This is way the Scheduling and Optimization team of any refinery needs to keep any eye of these fluctuations and take appropriate tuning actions on this schedule throughout the month of consideration.

Table 8 Variables listing



Monthly Optimization Programming

Variable/Commodity Description		**Variable Name**	**Value (mt)**	**Cost '1000$**
FCC naphtha x1	95domestic	x1dom95	5.193	4.155
	98domestic	x1dom98	5.201	4.160
	100domestic	x1dom100	1.375	1.100
	95export	x1exp95	12.400	9.920
Isomerate x2	95domestic	x2dom95	6.480	5.475
	98domestic	x2dom98	1.455	1.230
	100domestic	x2dom100	66	56
	95export	x2exp95	9.286	7.846
LSR x3	95domestic	x3dom95	4.716	2.806
	98domestic	x3dom98	4.215	2.508
	100domestic	x3dom100	270	161
	95export	x3exp95	5.973	3.554
Reformate x4	95domestic	x4dom95	16.813	14.207
	98domestic	x4dom98	13.414	11.335
	100domestic	x4dom100	2.306	1.949
	95export	x4exp95	27.467	23.209
TRN x5	95domestic	x5dom95	0	0
	98domestic	x5dom98	0	0
	100domestic	x5dom100	0	0
	95export	x5exp95	0	0
Butane x6	95domestic	x6dom95	1.254	652
	98domestic	x6dom98	1.085	564
	100domestic	x6dom100	238	124
	95export	x6exp95	2.422	1.259
MTBE x7	95domestic	x7dom95	0	0
	98domestic	x7dom98	3.964	3.956
	100domestic	x7dom100	744	743
	95export	x7exp95	292	291
ETBE x8	95domestic	x8dom95	1.335	1.666
	98domestic	x8dom98	665	830
	100domestic	x8dom100	0	0
	95export	x8exp95	0	0
Alkylate x9	95domestic	x9dom95	0	0
	98domestic	x9dom98	0	0
	100domestic	x9dom100	0	0
	95export	x9exp95	2.161	2.151
Unl95 dom		ydom95	35.791	30.959
Unl98 dom		ydom98	30.000	27.150
Unl100 dom		ydom100	5.000	4.725
Unl95 exp		yexp95	60.000	48.900
	Objective Function (Maximize Revenue)			**5.827**

The variables need to take values that meet the constraints of the optimization problem. The constraints are:

- Quality requirements of products ydom95/ydom98/ydom100/yexp95. In the below excel table the constraints related to commercial specs of Unleaded 95Ron for domestic market are presented. Quality constraints, as input in the model, will be registered for the other selling products, likewise.

Table 9 Quality associated constraints

Constraints I - Quality Requirements/Specs			
rvp winter max	79,8032	<	80
rvp winter min	79,8032	>	50
final boiling point max	169,2419	<	210
ron min	95,0000	>	95
mon min	85,0000	>	85
slphur max	4,0513	<	10
density max	0,7381	<	0,775
density min	0,7381	>	0,72
evap @70C max	35,9954	<	50
evap @70C min	35,9954	>	22
evap @100C max	52,5804	<	71
evap @100C min	52,5804	>	46
evap @150C min	84,9831	>	75
aromatics max	34,6590	<	35
benzene max	1,0000	<	1
O2 content max	0,0869	<	2,7
VLI	1050,0000	<	1050

Basis to below product's specs:

Table 10 Products Specifications

	ydom95	ydom98	ydom100	yexp95
RVPtot, psi	(Sum/Win)	(Sum/Win)	(Sum/Win)	(Sum/Win)
RVPtot, Kpa	45-60 / 50-80	45-60 / 50-80	45-60 / 50-80	45-60 / 50-80
Vapour Lock Index	1050 max	1050 max	1050 max	1050 max
FBP	210 max	210 max	210 max	
Evaporated @70 C, vol%	(20-48/22-50)	(20-48/22-50)	(20-48/22-50)	
Evaporated @100 C, vol%	46-71	46-71	46-71	
Evaporated @150 C, vol%	75 min	75 min	75 min	
ACTUAL RON				
ACTUAL MON				
Δ (RON-MON)				
RON Bonus				
MON Bonus				
RON prediction	95 min	98 min	100 min	95 min
MON prediction	85 min	86 min	87 min	85 min
Sulfur (%wt.)	10 ppm max	10 ppm max	10 ppm max	10 ppm max
Aromatics (%vol)	35% max	35% max	35% max	35% max
Ethers (%vol)	~15 % max	~15 % max	~15 % max	10 % max
Density (g/ml)	0.72-0.775	0.72-0.775	0.72-0.775	0.72-0.775
Benzene (%vol)	1% max	1% max	1% max	1% max
O2 (%wt)	2.7% max	2.7% max	2.7% max	2.5% max

At this stage we need to discuss in detail how the value of each attribute is calculated on the blended product. There are two kind of attributes; those that are getting mixed in a linear way, either in terms of volume or in terms of mass and those which don't follow linearity when they are getting mixed. If we need to blend linearly in terms of volume we use the density of each stream to convert the mass to volume and we switch back to mass appropriately, in the cases that we need to follow linear blending operation in terms of mass. In the following table we present the blending rules we have used in approaching the gasoline blending optimization problem.

Table 11 Linear/Non-linear blending "behaviours" of attributes

RVPIndex	FBP	Evaporated @70 C, vol%	Evaporated @100 C, vol%	Evaporated @150 C, vol%	RON prediction	MON prediction	Sulfur (%wt.)	Aromatics (%vol)	Ethers (%vol)	Density (g/ml)	Benzene (%vol)	O2 (%wt)	Bio-ethers (%vol)	Olefins (%vol)
linear vol	linear vol	linear vol	linear vol	linear vol	linear vol	linear vol	linear wt	linear vol	linear vol	linear vol	linear vol	linear wt	linear vol	linear vol

- The second major category of constraints are the mass balances related constraints and those subject to operational limitations of the refinery processes. Mass balances related constraints, as discussed already, dictate that the total quantity of different blending streams on every blending mode should match the quantity of each final product. Another operational constraint is that all variables should be positive numbers and take values lower than the maximum storage capacity allocated to them by the refinery's personnel. We suppose that during the design stage of refinery's tank farm implementation, the appropriate tankage space has been allocated for the intermediate streams storage, either if they're coming out of the production sequence of the refinery or if they're being imported from the Supply and Trading Division. Regarding final products we must set two set of operational limitations. One set is the minimum quantity for each one that needs to be produced in order to meet the market demand. The second set is again the tankage space available to store the final products and move respective stock to the following month. To simplify the problem, in our case, we have not taken into account the stock level (for streams and products alike) accumulation from the preceding month.

Table 12 Constraints listing

Constraints II - Mass Balances & Operational Restrictions			
Demand for Unl95 domestic	35.791	>	30.000
Demand for Unl98 domestic	30.000	>	10.000
Demand for Unl100 domestic	5.000	>	2.000
Demand for Unl95 exp	60.000	>	60.000
Mass balance blender for Unl95 dom	35.791	=	35.791
Mass balance blender for Unl98 dom	30.000	=	30.000
Mass balance blender for Unl100 dom	5.000	=	5.000
Mass balance blender for Unl95 exp	60.000	=	60.000
FCC naphtha blending stream availability	24.168	<	100.000
Isomerate blending stream availability	17.287	<	60.000
LSR blending stream availability	15.174	<	60.000
Reformate blending stream availability	60.000	<	60.000
TRN blending stream availability	0	<	60.000
Butane blending stream availability	5.000	<	5.000
MTBE blending stream availability	5.000	<	5.000
ETBE blending stream availability	2.000	<	5.000
Alkylate blending stream availability	2.162	<	5.000
Storage capacity Unl95 domestic	35.791	<	60.000
Storage capacity Unl98 domestic	30.000	<	30.000
Storage capacity Unl100 domestic	5.000	<	5.000
Storage capacity Unl95 exp	60.000	<	100.000
ETBE min requirement in domestic sales	2.000	>	2.000

The problem is completely parameterized. The basic parameters are:

- availability of blending streams
- availability of products storage
- demand of the products
- selling prices and blending components cost

Apart from the prices that fluctuate daily and determine the objective function of our model, other parameters can drastically change during the month of analysis. That might be the demand on a specific product or the tankage space due to unscheduled tank maintenance reasons or the availability of a blending stream due to production shortfalls or due to unavailability of an imported blending component, etc. For all these reasons the Scheduling and Optimization Division of the refinery needs to be alert and closely follow the implementation of the model results. In reality, it's not rare the refinery staff to take actions and align model's monthly outcome with the aforesaid modifications. Of course, the above gasoline production scheme is being revisited often, even on a weekly basis, depending upon each refinery's resources, for fine tuning modifications related to the fluctuation of the prices and/or demand.

MODELLING RESULTS

Using "Solver" subroutine of Microsoft Excel we have analyzed the above optimization problem. We have set the demands and stream availabilities as stated in the right hand side column of the above table "Constraints II – Mass Balances and operational Restrictions". Solver's results are:

Table 13 Model's Results

Objective Cell (Max)

Cell	Name	Original Value	Final Value
E46	Objective Function (Maximize Revenue) '1000$	12.118	5.827

Variable Cells

Cell	Name	Original Value	Final Value	Integer
D5	x1dom95 Value (mt)	1.000	5.193	Contin
D6	x1dom98 Value (mt)	1.000	5.201	Contin
D7	x1dom100 Value (mt)	1.000	1.375	Contin
D8	x1exp95 Value (mt)	1.000	12.400	Contin
D9	x2dom95 Value (mt)	1.000	6.480	Contin
D10	x2dom98 Value (mt)	1.000	1.455	Contin
D11	x2dom100 Value (mt)	1.000	66	Contin
D12	x2exp95 Value (mt)	1.000	9.286	Contin
D13	x3dom95 Value (mt)	1.000	4.716	Contin
D14	x3dom98 Value (mt)	1.000	4.215	Contin
D15	x3dom100 Value (mt)	1.000	270	Contin
D16	x3exp95 Value (mt)	1.000	5.973	Contin
D17	x4dom95 Value (mt)	1.000	16.813	Contin
D18	x4dom98 Value (mt)	1.000	13.414	Contin
D19	x4dom100 Value (mt)	1.000	2.306	Contin
D20	x4exp95 Value (mt)	1.000	27.467	Contin
D21	x5dom95 Value (mt)	1.000	0	Contin
D22	x5dom98 Value (mt)	1.000	0	Contin
D23	x5dom100 Value (mt)	1.000	0	Contin
D24	x5exp95 Value (mt)	1.000	0	Contin
D25	x6dom95 Value (mt)	1.000	1.254	Contin
D26	x6dom98 Value (mt)	1.000	1.085	Contin
D27	x6dom100 Value (mt)	1.000	238	Contin
D28	x6exp95 Value (mt)	1.000	2.422	Contin
D29	x7dom95 Value (mt)	500	0	Contin
D30	x7dom98 Value (mt)	500	3.964	Contin
D31	x7dom100 Value (mt)	500	744	Contin
D32	x7exp95 Value (mt)	500	292	Contin
D33	x8dom95 Value (mt)	500	1.335	Contin
D34	x8dom98 Value (mt)	500	665	Contin
D35	x8dom100 Value (mt)	500	0	Contin
D36	x8exp95 Value (mt)	500	0	Contin
D37	x9dom95 Value (mt)	500	0	Contin
D38	x9dom98 Value (mt)	500	0	Contin
D39	x9dom100 Value (mt)	500	0	Contin
D40	x9exp95 Value (mt)	500	2.161	Contin
D41	ydom95 Value (mt)	10.000	35.791	Contin
D42	ydom98 Value (mt)	10.000	30.000	Contin
D43	ydom100 Value (mt)	10.000	5.000	Contin
D44	yexp95 Value (mt)	10.000	60.000	Contin

We managed to maximize revenue at $5.827.000 by producing:

Unleaded 95Ron for domestic market	35.791 MT
Unleaded 98Ron for domestic market	30.000 MT
Unleaded 100Ron for domestic market	5.000 MT
Unleaded 95Ron for exports	60.000 MT

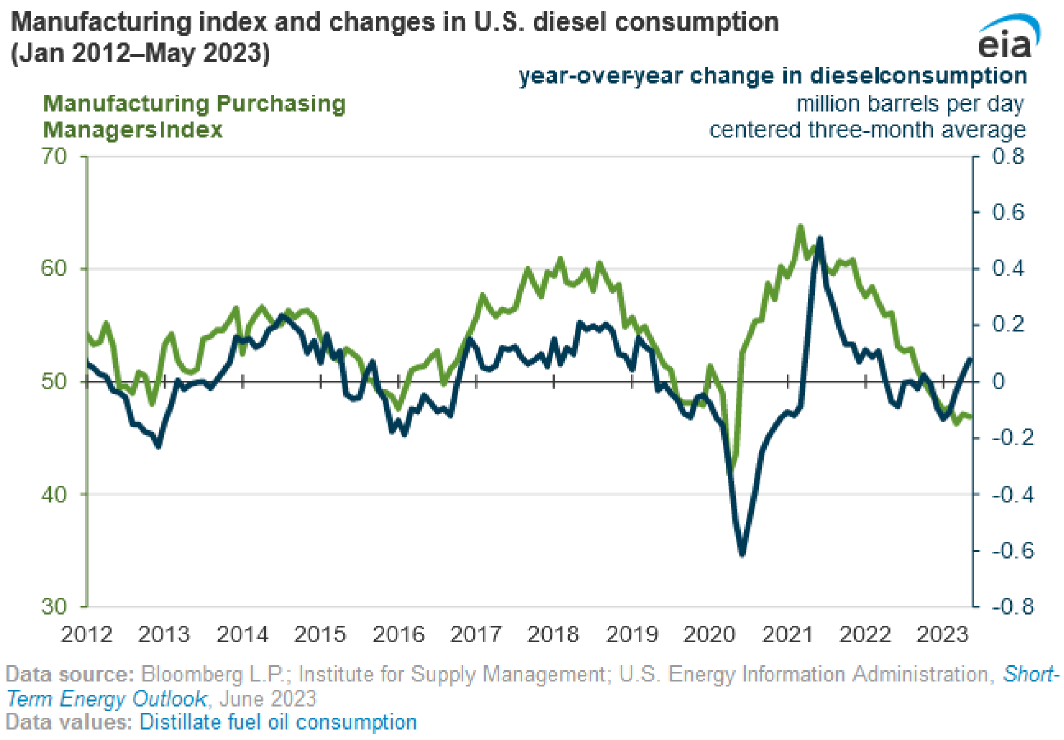
CHAPTER 2 – DIESEL CHARACTERISTICS AND BLENDING OPTIMIZATION ANALYSIS

INTRODUCTION

Diesel fuels are critical to the humanity since they keep the world economy moving. Consumer goods to move around the world by road or by sea, electricity generation to give electric power to households and businesses of the globe, efficiency increase on farms or other agricultural sectors and hundreds of others applications of global economy are completely dependent on diesel fuel. The principal uses of diesel fuel are:

- On-road transportation
- Farming
- Marine shipping
- Electric Power generation
- Off-road uses (mining, construction, logging, etc)
- Military transportation/usage
- Rail transportation

Because diesel is used to move goods from manufacturers to consumers, diesel's sales is a decent indicator strongly related to the strength of the economy. Historically, one country's GDP is strongly correlated to its manufacturing production. The same applies to US economy, as being schematically described by the following graph for the preceding decade:


Manufacturing index and changes in U.S. diesel consumption (Jan 2012–May 2023)

Data source: Bloomberg L.P.; Institute for Supply Management; U.S. Energy Information Administration, *Short-Term Energy Outlook*, June 2023
Data values: Distillate fuel oil consumption

Figure 12 Manufacturing Index compared to Diesel Consumption

DIESEL AND ITS CHARACTERISTICS

Diesel, also called petroleum diesel or petrodiesel or fossil diesel is the most common type of diesel fuel. It's produced by fractional distillation of crude oil between 200°C and 350°C at atmospheric pressure, resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule. Fossil diesel is composed of about 75% saturated HCs (paraffins, including n-, iso- and cycloparaffins) and 25% aromatic HCs (including naphthalenes and alky benzenes). The average chemical formula for common diesel fuel is $C_{12}H_{23}$, ranging approximately from $C_{10}H_{20}$ to $C_{15}H_{28}$. Petroleum is a useful chemical substance for many important purposes, but it is also a nonrenewable resource with a highly toxic composition. It poses significant problems when used in huge volumes throughout the industrialized world.

Early diesel engines were large, ineffective, running in low speed and requiring low quality fuel. As the engines were being improved, they became lighter and capable of higher speed, the viscous, heavy fuel had to be replaced by a lighter, good quality fuel. The diesel quality and engine parameters determine the introduction of fuel into the combustion chamber, the mixture forming, and the ignition and as a result the combustion characteristics and the emission properties.

The properties of diesel affect:

- Mixture forming
- Ignition and combustion processes
- Performance
- Lubricating Oil
- Environment and emission

Therefore, the critical properties of diesel fuel are:

- Density and energy content
- Distillation
- Chemical composition (stability, corrosion effect, lubricity, cold flow)

Less critical properties are:

- Viscosity
- Foam formation
- Flashpoint
- Coking ability
- Electrical conductivity

Ignition delay can be attributed to engine's design, operating conditions and the cetane number of diesel. Diesel with a lower cetane number causes higher ignition delay. That means delayed cold starting, consequently higher emissions, often as "white smoke" and engine noise caused by higher pressure peaks. With higher cetane number fuel, engine runs in hot operation, the combustion is better and smoother and the emissions are kept lower, the producing engine noise is kept lower and consequently the engine's life is notably extended.

The cetane number depends on hydrocarbon composition: the more paraffinic and lower aromatic compounds are present in the fuel the higher the cetane number. The value of cetane number, still, can be improves by appropriate additives.

The **density of the fuel** influences directly the volumetric energy content, which in turn influences the driving experience. With higher density and the same injection volume, engine gives higher performance and the acceleration will be higher. With increase in the density particle emission increases, but at the same time the volumetric fuel consumption decreases, if the car manufacturer has set a maximum injection volume. A decrease of density occurs the opposite.

A basic parameter of diesel fuel is the **distillation curve**, which is a curve of boiling points. Because it's a mixture of hydrocarbons, it cannot be characterized by a single boiling point, but with a boiling range and by some temperature data related to the amount of distilled fraction. A typical distillation curve of a diesel gasoil is shown in figure 17.

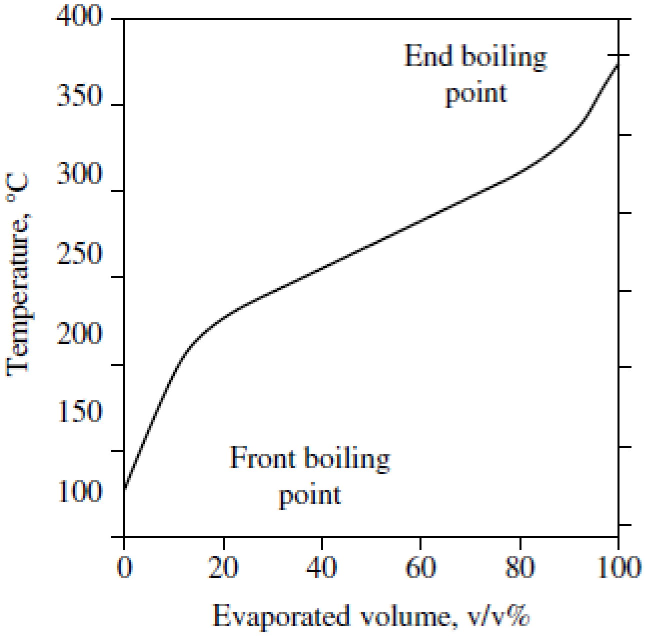


Figure 103 Typical Distillation Curve of Diesel

The boiling range basically affects other properties such as viscosity, density, ignition, flashpoint and flow at low temperatures. One of the preferred points of the curve is the initial boiling point, which is closely related to the flashpoint as being a safety requirement. Therefore, the initial boiling point should be at least as high as the closed-cup measurement of flash point, 55-60°C. The amount of lighter components in diesel is regulated by the initial boiling point and the flashpoint.

The fraction distillated below 250°C is responsible for the low density and energy content; the boiling fraction up to 350°C and higher, up to 370°C (at least 85% and 95%) sets the limit for the heavier components. Fractions in this temperature range contain polynuclear aromatics in high concentration and are mainly responsible for particulate emissions. They also ease the formation of carbonaceous deposits on the nozzles. At the top of the boiling range, the concentration of the higher molecular weight n-paraffins can be so high that they degrade the cold flow properties of the product (e.g. pour point, cold filter plugging point: CFPP). It is validated experimentally that a distillation point of 90% v/v correlates well with the freezing point as an independent variable, pour point with the concentration of C_{22} - C_{23} n-paraffins and the CFPP with the two previous independent variables (Hancsók, J. (1999). Modern Engine and Jet Fuels. II. Diesel Fuels, Veszprém University Press, Veszprém).

The **chemical composition** of diesel determines several important properties, such as ignition and combustion properties, the density, the energy content and the shape of the distillation curve. The chemical composition of diesel also affects the stability, the corrosive effects, the low temperature flow properties and the composition of the gas mixture formed during the combustion and so the emissions.

Oxidation stability of diesel is a serious problem for consumers and engine manufacturers. Diesel can only partially oxidized and polymerized, so rubber-like materials (often insoluble resins) and their precursors are formed. These substances are responsible for forming deposits in the fuel system, which causes the fouling of filters and if they are transmitted through the filter, they can form deposits on the upper cylinder wall of the engine and on the nozzles. These resin deposits certainly decrease engine's performance, impair driving and increase emissions as well.

The stability of diesel depends on:

- Fuel composition. The production technology of the blending output is the main factor. FCC gasoil and Cocker gasoil not sufficiently hydrogenated contain a lot of unsaturated, aromatic and heteroatomic compounds, unlike hydrocracked gasoil.

- Storage conditions. The tank's construction (fix or floated roof), the presence of metals and metal-oxides, the ambient and storage temperature and the duration of storage are all important factors.

Corrosion Properties. Diesel comes in contact with the metallic structural parts of vehicles but they must not exert a corrosive effect on them. Pure hydrocarbons are non-corrosive but the presence of acidic and active sulphur-containing compounds in gasoil, makes them aggressive towards copper and its alloys and can cause significant "wear", especially at long shutdowns. With long-term storage in changing temperatures, water condensation can corrode tank walls. The corrosion can be prevented by applying anticorrosion additives.

Nonetheless, in engine and exhaust system corrosion cannot be prevented with additives, since it is brought by the acidic compounds (sulphur dioxide, sulphur trioxide, nitrogen oxides, other acids) formed during the combustion of sulphur and nitrogen-containing compounds. These can reduce the level of engine oil, under certain conditions and contribute consequently to the formation of the acid rains and the ozone depletion. Furthermore, these combustion products decrease remarkably the activity of after-treatment catalysts. That's the reason that sulphur content was drastically reduced in recent years. In particular, in US ultralow sulfur diesel with a maximum of 15 ppm sulfur has been the norm since 2006 for on-road vehicles, 2010 for non-road vehicles and 2012 for locomotives and marine vessels. Correspondently, mandatory environmental directives issued by the European Union as well as industry standards developed by the European Standards Organization (CEN) clearly impose 10ppm sulphur limits in diesel and gasoline since 2009 (for on-road vehicles) and 2011 (for non-road vehicles) (www.transport policy.net).

The nitrogen content has not been restricted, yet. The reason for that might be that deep hydrodesulfurization takes place with the reduction of the nitrogen content. Some countries are, however, setting up standards to limit the nitrogen content.

Lubricating Properties. Due to the decrease in sulphur and nitrogen content and the reduced concentration of polar compounds (aromatics), diesels appear significant loss of lubricity. This has a direct effect in the wear to the cam disc of the injection pump and the injector.

The high cetane number is mainly attributed to straight-chain paraffinic hydrocarbons. But these formations adversely affect the cold flow properties of diesel, because they have high freezing point caused by crystals formations. These crystals are large enough to hinder pumping, to block up the fuel filters and to settle in the tanks. To prevent these effects special additives can be used. The **cold flow properties** commonly reported are the following:

- Cloud Point: Immersion temperature of raw materials paraffinic hydrocarbon crystals (waxes)
- Pour Point: The lowest temperature that fuel can be pumped
- Cold Filter Plugging Point (CFPP):The temperature in which the fuel does not pass through one grid in less than 60 sec

THE BLENDING PROBLEM

Diesel gasoils are blended from desulphurized gasoil streams, from desulphurized and dewaxed" gasoil streams, or from desulphurized, dearomatized, and "dewaxed" gasoil streams. The gasoil boiling points range is based on the ratios of three components:

- Biodiesels
- Biogas oils
- Fischer–Tropsch gasoils

The blending process is followed by the admixture of additives or additive packages. It is possible that before this final blending some additives have already been introduced into the blending component streams (e.g. flow improvers, stabilizers) for reasons of easier storage and handling.

The ratios of the most important properties – density, cetane number, sulphur content are illustrated in the below two graphs:

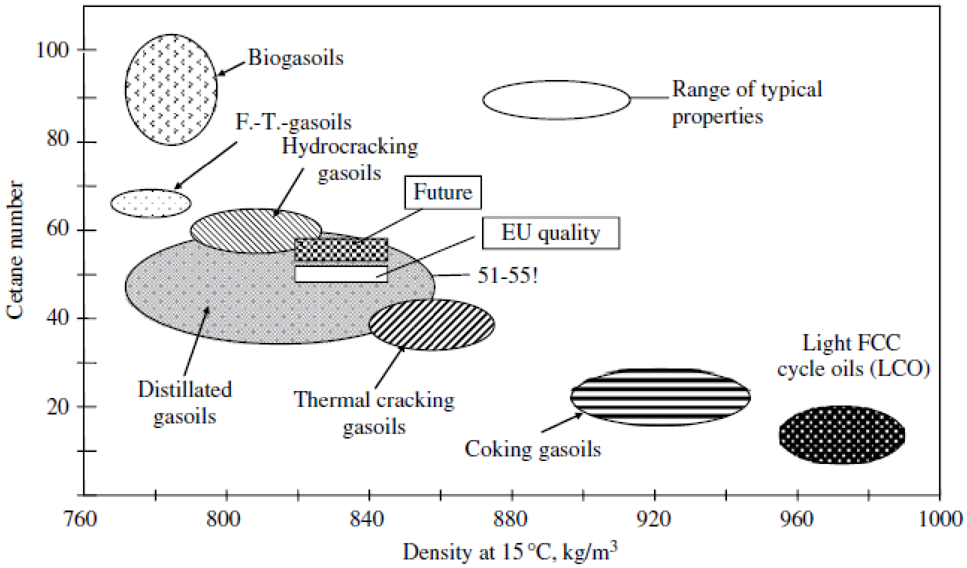


Figure 114 Gasoil's density and ketane number variation

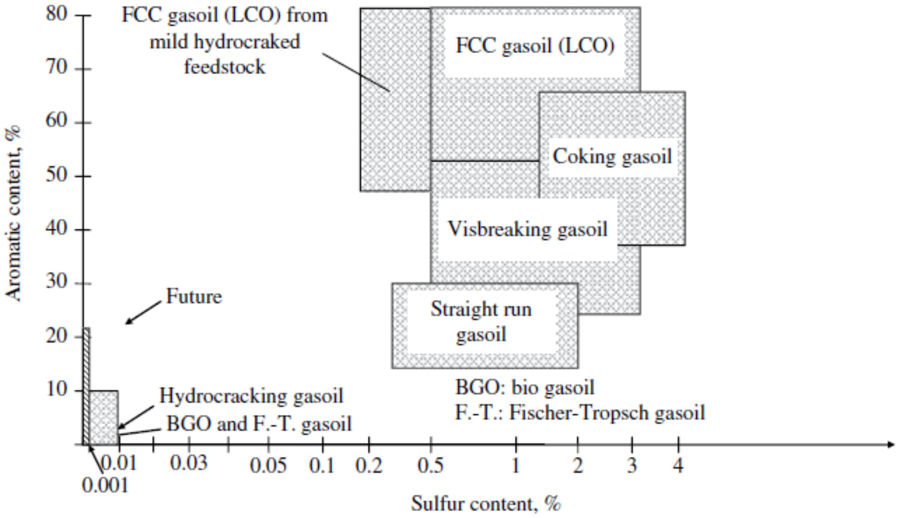


Figure 15 Gasoil's sulphur & aromatic content varies

The blending optimization, as discussed also in gasoline blending optimization problem, is carried out at minimal production cost in order to maximize profits. Two principals are followed by a complex refinery. First, the ratio of blending components is set in the blending system so that the quality properties of mixture are specified at the entrance of storage tank. Second, the quantity ratios of the blending components are chosen so that the given quality properties of the fuel mixture are reached at the point of filling the storage tank. A modern blending facility scheme is being supervised by an integrated computerized technology package with the following main components:

- Interface of monthly linear programmed refinery models for middle-range recipes
- Timing system for optimizing future products and blending orders
- Online multivariate control and optimization system for feedback from control equipment to enable inline certification and transport of goods

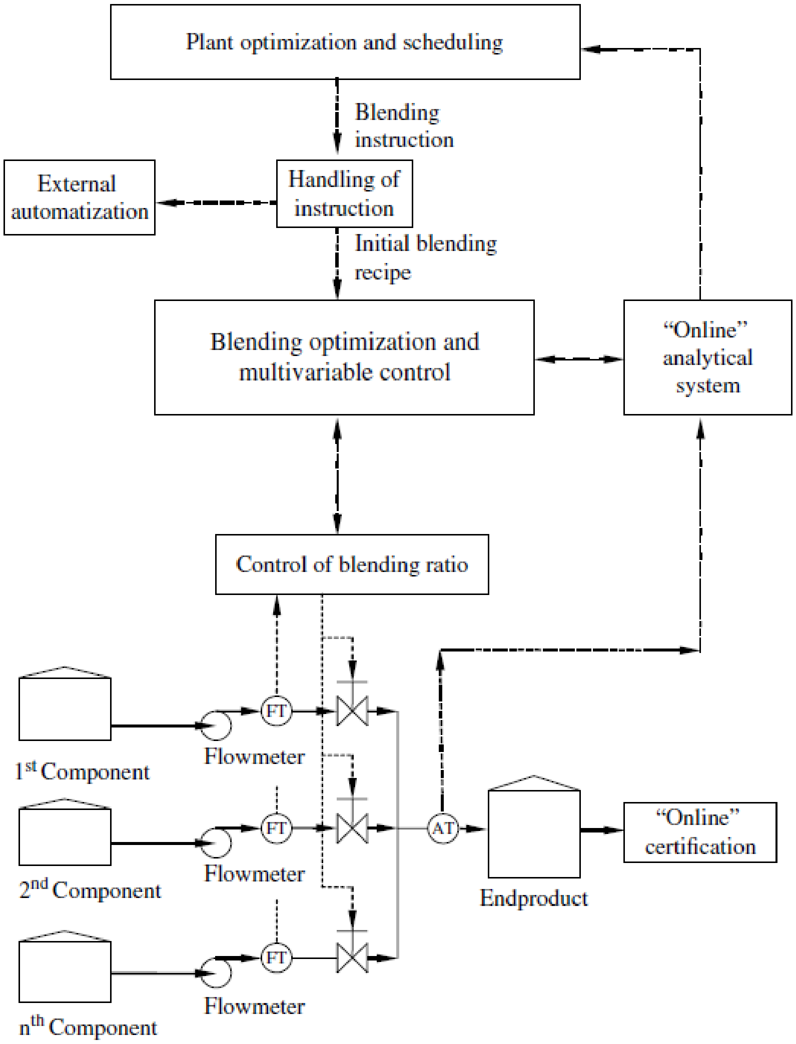
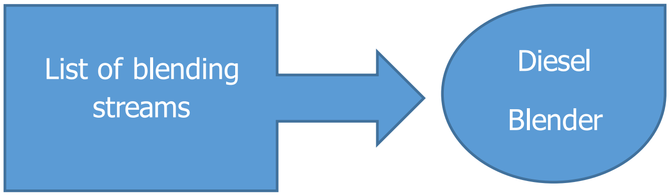


Figure 126 Management and control of fuel blending

In a highly complex refinery the most commonly employed streams in diesel auto production are presented below:



1. Straight Run Gasoil (SRGO)
2. FCC Light Cycle Oil (LCCO)
3. Heavy Gasoil (HGO)
4. Hydrocracked Gasoil (HCGO)
5. Coker Light Gasoil (LKGO)
6. Kerozene Light Sulphur (LSKERO)

Therefore the blending problem comprises the blending of above streams to that extent that the objective function of overall revenue of the sale of final products minus the cost of above blending streams will be maximized.

BLENDING STREAMS - A TECHNICAL REVIEW

LIGHT CYCLE OIL

Conversion processes perform chemical reactions that “crack” large, high-boiling hydrocarbons into smaller, lighter molecules suitable for blending purposes towards high-value light products. The conversion processes of principal interest are fluid catalytic cracking (FCC), Hydrocracking and Coking.

FLUID CATALYTIC CRACKING (FCC)

Offers:

1. High yields of gasoline and distillate material (range of 60-75vol% on feed)
2. High reliability and low operating costs
3. Flexibility to handle changes in crude slate processing quality and refined products quality alike.

It’s remarkable to say that in a large, transportation fuels oriented refinery, the FCC unit accounts for more than 40% of the total refinery output of gasoline and diesel fuels.

FCC also produces large amount of light gases (C_1 to C_4), including olefins. Olefins are valuable substances either as petrochemical feedstocks or as feedstocks to refinery's upgrading processes. With suitable catalyst selection and operating conditions FCC unit can be designed to maximize production of gasoline blend stock (FCC naphtha), distillate blend stock (Light cycle oil – LCO) or petrochemical feedstocks.

Sulphur is the worst enemy of FCC catalysts, since contact with sulphur reduces their effectiveness. For this reason major refineries commonly use desulphurization units in front of FCC to remove that "poison" from its feed. Even in such process sequence in place the streams produced by the FCC still contain some sulphur. Indeed, untreated FCC products, like FCC naphtha and light cycle oil) are the primary sources of sulphur in transportation fuels.

HYDROCRACKING

Converts distillates and gasoils from crude distillation primarily to gasoline and diesel, similarly to FCC. It's a catalytic process that operates at medium temperature and high pressure. It applies externally-generated hydrogen to crack distillate and heavy gas oil feeds into light gases, petrochemical feedstocks and gasoline and diesel fuel blend stocks. Like FCC, hydrocracking offers high yields of light products and extensive operating flexibility. Product yields from hydrocracking depend on how the unit is designed and operated. At one operating extreme, a hydrocracker can convert essentially all of its feed to gasoline blend stocks, with yields about 100%vol on feed. Alternatively, a hydrocracker can produce jet fuel and diesel fuel, with combined yields of 85% to 90%vol, along with small volumes of gasoline material. Hydrocracking has a notable advantage over FCC; the hydrogen input to the hydrocracker not only leads to cracking reactions but also to other reactions that remove hetero-atoms –especially sulfur –from the hydrocracked streams. These "hydrotreating" reactions yield hydrocracked streams with very low sulfur content and other improved properties.

COKING

It's a thermal, non-catalytic conversion process, where residual oil, i.e. the heaviest residue from crude distillation, is cracked into lighter intermediates for further processing. In this way the "bottom of the crude barrel" is converted into valuable light products. These products comprise light gases (including light olefins), low quality naphtha (coker naphtha), distillate streams (coker distillate) for further treatment and large amount of coker gasoil and petroleum coke (abt 25-30wt% on feed). The coker gasoil is used mainly as additional FCC feed. However, coker gasoil contains high levels of sulphur and other contaminants, which make it less desired as FCC feed compared to straight run gasoil streams.

As we have already mentioned the blending recipes are driven by the product's specifications and the availability of the blending components at the time of resolving the blending/production optimization exercise within a refinery. These recipes are fine-tuned by the commercial and operational conditions that prevail in the specific geographical area under consideration.

For instance, Greece, following European Union's legislation, before 2005 needed to supply the domestic market with Gasoil, used for heating purposes in the majority of central heating boilers, in the rural and urban population alike and automotive diesel with the same specification in regard to Sulphur content, i.e. max 0.1% or 1000ppm. Once EU shifted to Euro 4 (Directive 98/70/EC) from January 2005 that made mandatory max Sulphur content 50ppm and soon after to Euro 5 (Directive 2003/17/EC) from January 2009, setting respective upper limit at 10ppm, it was extremely difficult for a refinery operating in the neighbor to use many "cheap" intermediate streams to produce ULSD (Ultra Low Sulphur Diesel) for transportation division. Profoundly, the reason was that most of the streams produced out of the refinery processes and were numerated before, have high concentration of Sulphur, minimizing the options for blending Diesel auto. Surely, the streams that can be used for Heating Gasoil production are more, since the max Sulphur mandate remains at 1000ppm.

As a result, a dominant Refinery Company in Greece (HelleniQ Energy Group) opts for two different set-ups to produce Diesel Auto. Aspropyrgos Refinery uses ULSD from the desulphurization units, Kerozene as produced from the Mild Hydrocracker and heavy naphtha produced out of FCC unit and after being hydro-treated. On the other side, Eleusis Refinery uses ULSD from the desulphurization units, Kerozene as produced by the High Pressure Section of Refinery's Hydrocracker, Gasoil as produced by the High Pressure Section of Hydrocracker and Gasoil as produced by the Low-Pressure Section of Hydrocracker. The above can be illustrated with the below graphs:

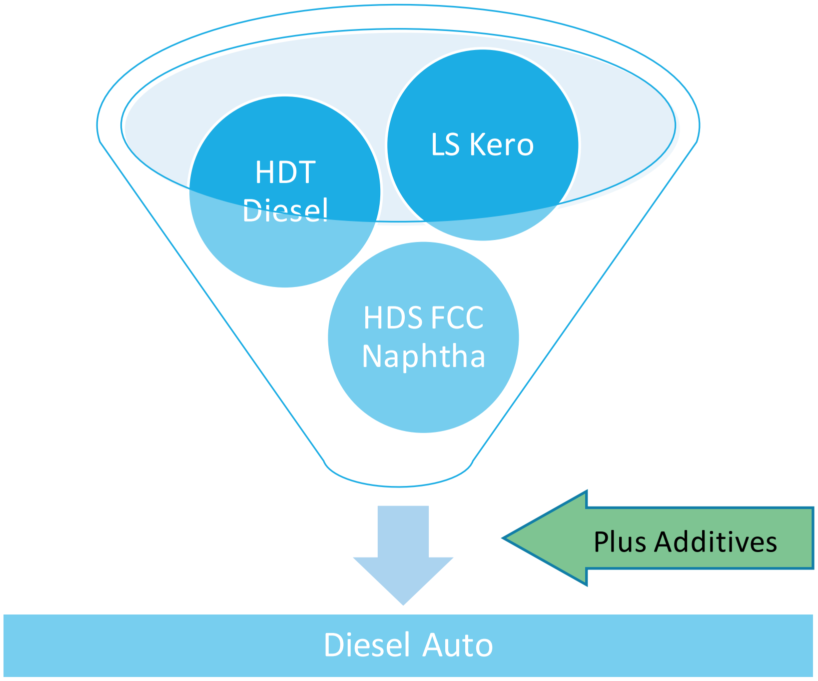


Figure 137 HelleniQ Energy Aspropyrgos Refinery - Diesel production set-up

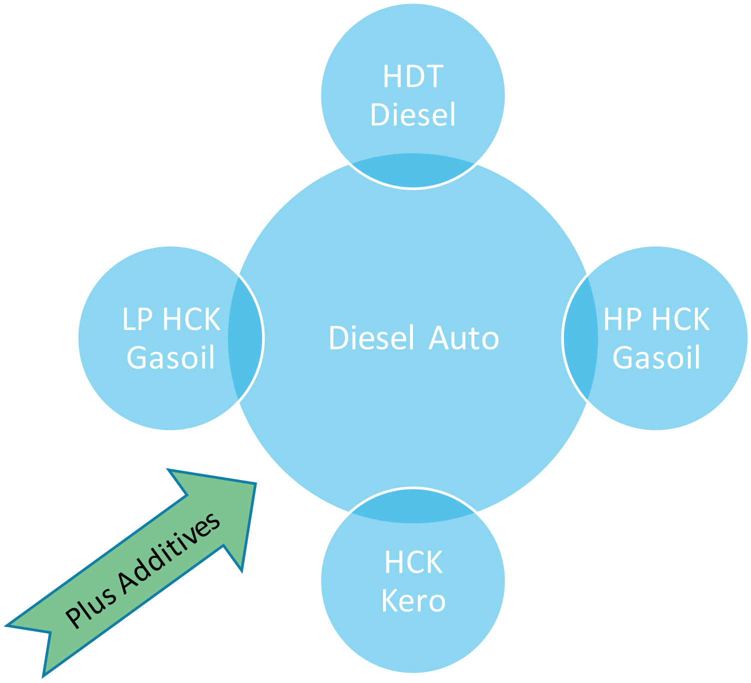
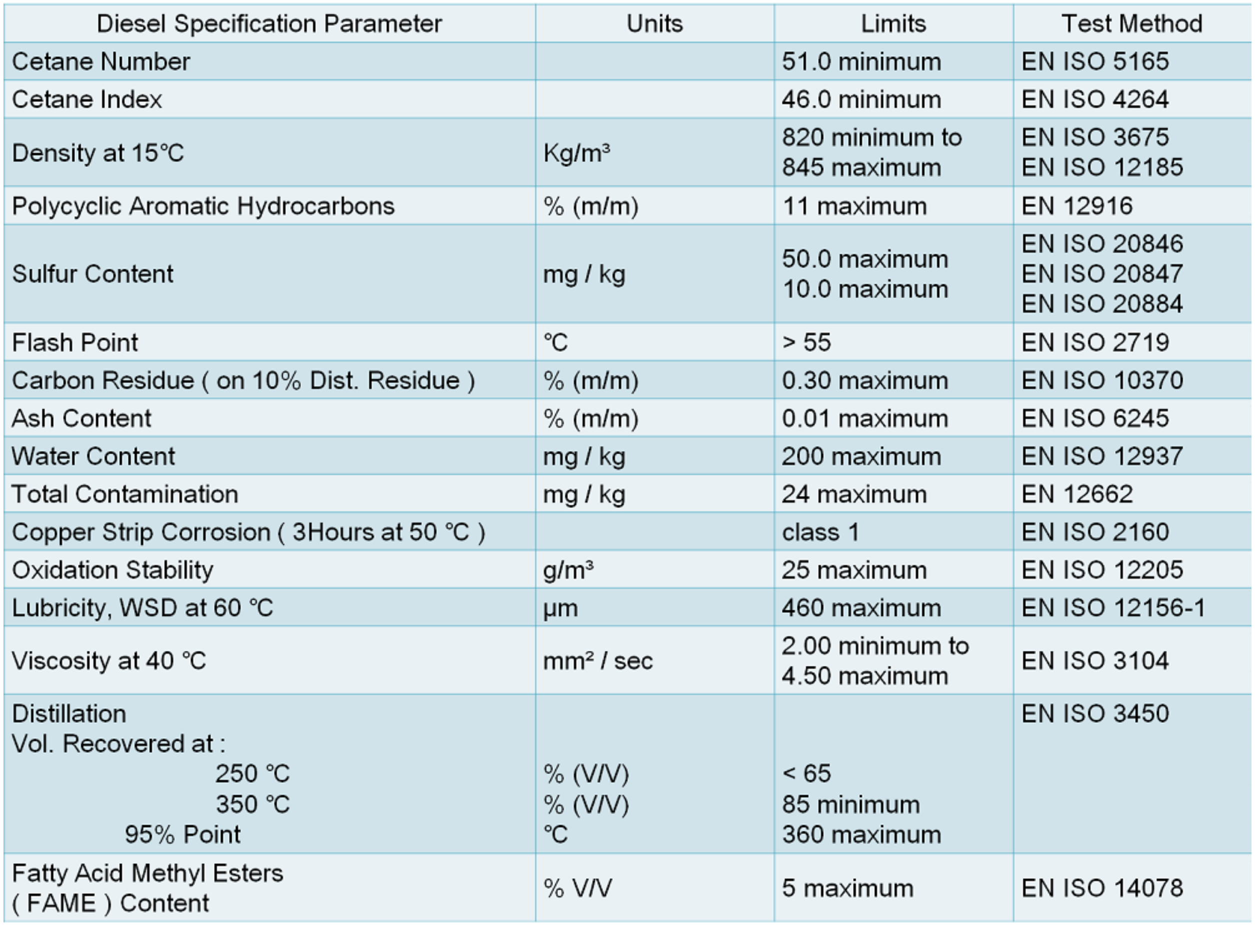


Figure 148 HelleniQ Energy Eleusis Refinery - Diesel production set-up

The principal attributes that need to be met, according to EN590, the dominant standard for domestic sales but also for export usage (whereas FAME content sometimes is not required) to the markets appealing to Greek diesel production, are the following:

Table 14 Diesel market specs



Diesel Specification Parameter	Units	Limits	Test Method
Cetane Number		51.0 minimum	EN ISO 5165
Cetane Index		46.0 minimum	EN ISO 4264
Density at 15℃	Kg/m³	820 minimum to 845 maximum	EN ISO 3675 EN ISO 12185
Polycyclic Aromatic Hydrocarbons	% (m/m)	11 maximum	EN 12916
Sulfur Content	mg / kg	50.0 maximum 10.0 maximum	EN ISO 20846 EN ISO 20847 EN ISO 20884
Flash Point	℃	> 55	EN ISO 2719
Carbon Residue (on 10% Dist. Residue)	% (m/m)	0.30 maximum	EN ISO 10370
Ash Content	% (m/m)	0.01 maximum	EN ISO 6245
Water Content	mg / kg	200 maximum	EN ISO 12937
Total Contamination	mg / kg	24 maximum	EN 12662
Copper Strip Corrosion (3Hours at 50 ℃)		class 1	EN ISO 2160
Oxidation Stability	g/m³	25 maximum	EN ISO 12205
Lubricity, WSD at 60 ℃	μm	460 maximum	EN ISO 12156-1
Viscosity at 40 ℃	mm² / sec	2.00 minimum to 4.50 maximum	EN ISO 3104
Distillation Vol. Recovered at :			EN ISO 3450
250 ℃	% (V/V)	< 65	
350 ℃	% (V/V)	85 minimum	
95% Point	℃	360 maximum	
Fatty Acid Methyl Esters (FAME) Content	% V/V	5 maximum	EN ISO 14078

As mentioned in gasoline blending chapter, some attributes of the blending components are behaving in a linear way, under the blending process – linearity can be achieved either in regard to mass or volume – whereas others' behavior is always far from the linear "pathway".

Table 15 Linear/Non-Linear Attributes

Density (g/ml)	Sulphur (%wt)	Evaporated @360 deg C, vol %	Flash Point, deg C	Pour Point / Cloud Point, deg C	Cetane Index	Cetane Number	Viscosity @50 deg C, cSt
linear vol	linear wt	linear vol	non-linear	non-linear	linear vol	linear vol	non-linear

One of the most convenient method of estimating properties, that are not blended linearly, is to substitute the true value of the property with another value, called blending factor or index, which behaves in a sense of linearity within blending process.

Flash Point

Regarding calculating the flash point of a mixture (blend) of two or more components, as a non-linear attribute, flash point blending indices need to be used, as conducted by Chevron Research Company and are presented here below.

The flash point index of a blend is given by the formulae: $(FPBI)_{blend} = \sum X_{vi} (FPBI)_i$,

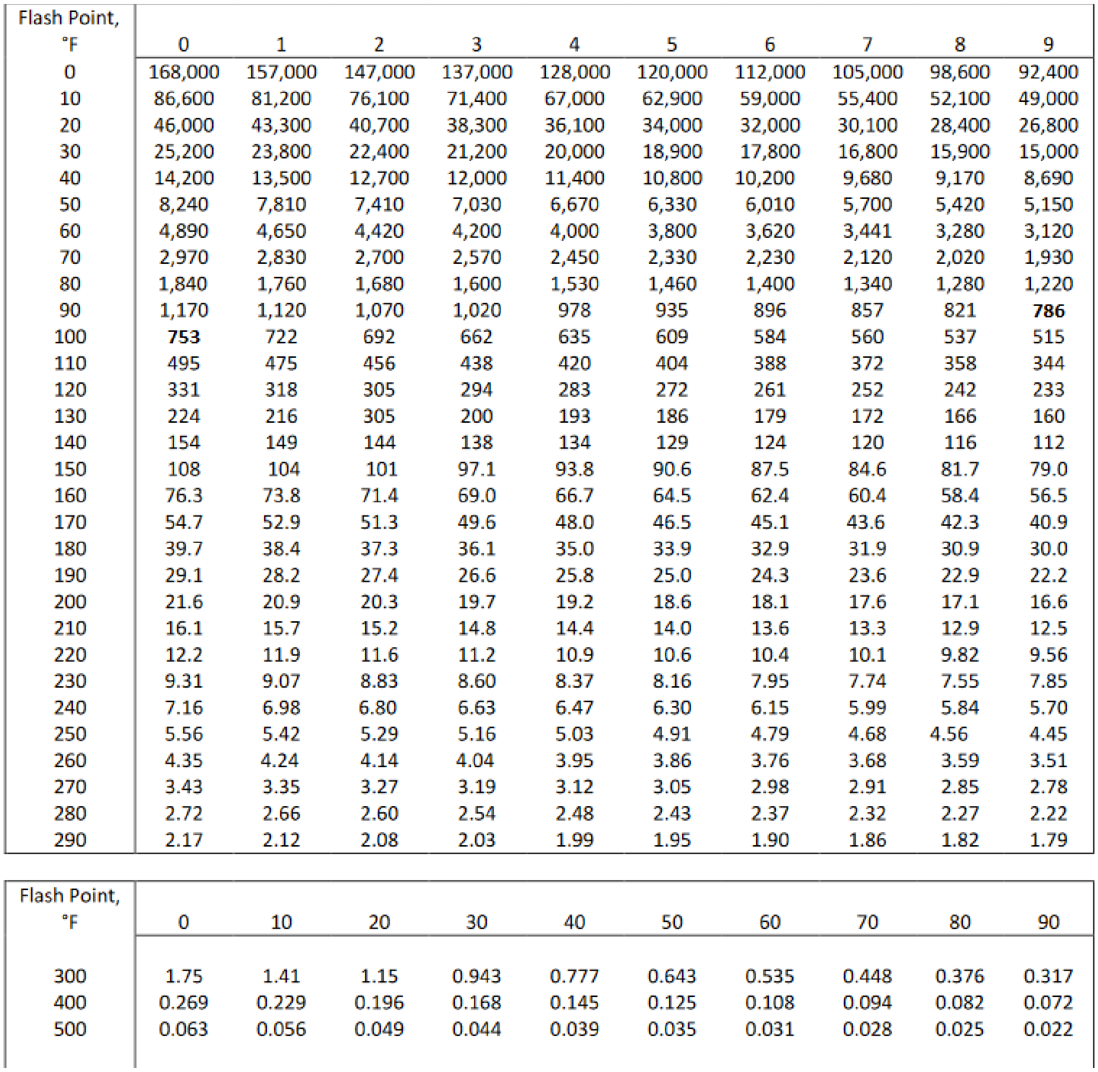
where:

X_{vi} = Volume fraction

$(FPBI)_{blend}$ = Flash point blending index of the blend

$(FPBI)_i$ = Flash point blending index of component I, as taken from below table

Table 16 Flash point blending index of component I



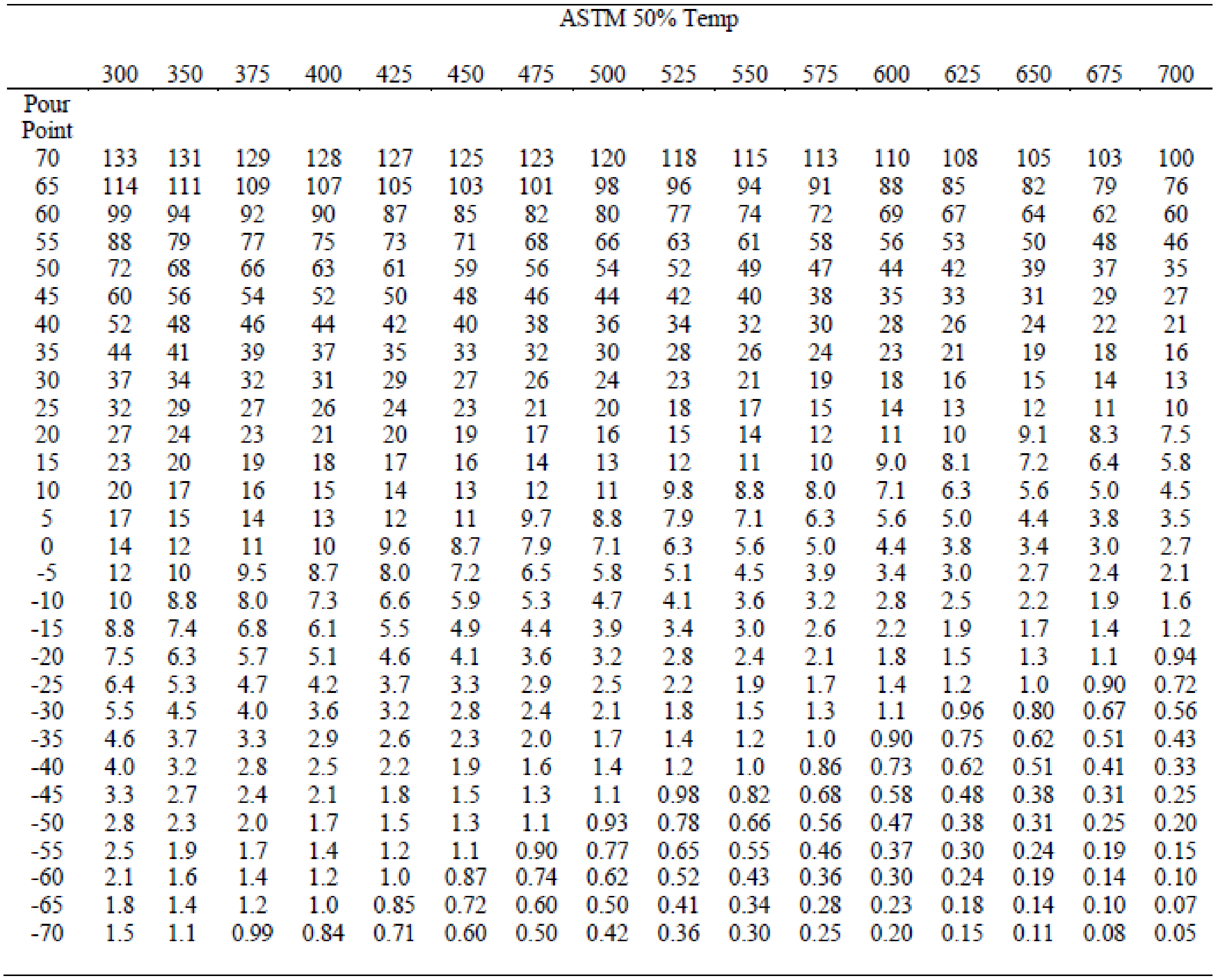
Flash Point, °F	0	1	2	3	4	5	6	7	8	9
0	168,000	157,000	147,000	137,000	128,000	120,000	112,000	105,000	98,600	92,400
10	86,600	81,200	76,100	71,400	67,000	62,900	59,000	55,400	52,100	49,000
20	46,000	43,300	40,700	38,300	36,100	34,000	32,000	30,100	28,400	26,800
30	25,200	23,800	22,400	21,200	20,000	18,900	17,800	16,800	15,900	15,000
40	14,200	13,500	12,700	12,000	11,400	10,800	10,200	9,680	9,170	8,690
50	8,240	7,810	7,410	7,030	6,670	6,330	6,010	5,700	5,420	5,150
60	4,890	4,650	4,420	4,200	4,000	3,800	3,620	3,441	3,280	3,120
70	2,970	2,830	2,700	2,570	2,450	2,330	2,230	2,120	2,020	1,930
80	1,840	1,760	1,680	1,600	1,530	1,460	1,400	1,340	1,280	1,220
90	1,170	1,120	1,070	1,020	978	935	896	857	821	**786**
100	**753**	722	692	662	635	609	584	560	537	515
110	495	475	456	438	420	404	388	372	358	344
120	331	318	305	294	283	272	261	252	242	233
130	224	216	305	200	193	186	179	172	166	160
140	154	149	144	138	134	129	124	120	116	112
150	108	104	101	97.1	93.8	90.6	87.5	84.6	81.7	79.0
160	76.3	73.8	71.4	69.0	66.7	64.5	62.4	60.4	58.4	56.5
170	54.7	52.9	51.3	49.6	48.0	46.5	45.1	43.6	42.3	40.9
180	39.7	38.4	37.3	36.1	35.0	33.9	32.9	31.9	30.9	30.0
190	29.1	28.2	27.4	26.6	25.8	25.0	24.3	23.6	22.9	22.2
200	21.6	20.9	20.3	19.7	19.2	18.6	18.1	17.6	17.1	16.6
210	16.1	15.7	15.2	14.8	14.4	14.0	13.6	13.3	12.9	12.5
220	12.2	11.9	11.6	11.2	10.9	10.6	10.4	10.1	9.82	9.56
230	9.31	9.07	8.83	8.60	8.37	8.16	7.95	7.74	7.55	7.85
240	7.16	6.98	6.80	6.63	6.47	6.30	6.15	5.99	5.84	5.70
250	5.56	5.42	5.29	5.16	5.03	4.91	4.79	4.68	4.56	4.45
260	4.35	4.24	4.14	4.04	3.95	3.86	3.76	3.68	3.59	3.51
270	3.43	3.35	3.27	3.19	3.12	3.05	2.98	2.91	2.85	2.78
280	2.72	2.66	2.60	2.54	2.48	2.43	2.37	2.32	2.27	2.22
290	2.17	2.12	2.08	2.03	1.99	1.95	1.90	1.86	1.82	1.79

Flash Point, °F	0	10	20	30	40	50	60	70	80	90
300	1.75	1.41	1.15	0.943	0.777	0.643	0.535	0.448	0.376	0.317
400	0.269	0.229	0.196	0.168	0.145	0.125	0.108	0.094	0.082	0.072
500	0.063	0.056	0.049	0.044	0.039	0.035	0.031	0.028	0.025	0.022

Pour Point

Pour point is also a non-linear attribute, that's why pour point blending indices were developed to allow reliable calculation of the pour point of the gasoil blends. Chevron Research Company has compiled the below table of pour point indices for a range of distillate fuels, where the blending indices are tabulated as a function of ASTM distillation curve 50% temperature in Fahrenheit, °F (1st horizontal listing) and pour point in Fahrenheit, °F (1st vertical listing) as well.

Table 17 Chevron's table of pour point indices



	ASTM 50% Temp															
Pour Point	300	350	375	400	425	450	475	500	525	550	575	600	625	650	675	700
70	133	131	129	128	127	125	123	120	118	115	113	110	108	105	103	100
65	114	111	109	107	105	103	101	98	96	94	91	88	85	82	79	76
60	99	94	92	90	87	85	82	80	77	74	72	69	67	64	62	60
55	88	79	77	75	73	71	68	66	63	61	58	56	53	50	48	46
50	72	68	66	63	61	59	56	54	52	49	47	44	42	39	37	35
45	60	56	54	52	50	48	46	44	42	40	38	35	33	31	29	27
40	52	48	46	44	42	40	38	36	34	32	30	28	26	24	22	21
35	44	41	39	37	35	33	32	30	28	26	24	23	21	19	18	16
30	37	34	32	31	29	27	26	24	23	21	19	18	16	15	14	13
25	32	29	27	26	24	23	21	20	18	17	15	14	13	12	11	10
20	27	24	23	21	20	19	17	16	15	14	12	11	10	9.1	8.3	7.5
15	23	20	19	18	17	16	14	13	12	11	10	9.0	8.1	7.2	6.4	5.8
10	20	17	16	15	14	13	12	11	9.8	8.8	8.0	7.1	6.3	5.6	5.0	4.5
5	17	15	14	13	12	11	9.7	8.8	7.9	7.1	6.3	5.6	5.0	4.4	3.8	3.5
0	14	12	11	10	9.6	8.7	7.9	7.1	6.3	5.6	5.0	4.4	3.8	3.4	3.0	2.7
-5	12	10	9.5	8.7	8.0	7.2	6.5	5.8	5.1	4.5	3.9	3.4	3.0	2.7	2.4	2.1
-10	10	8.8	8.0	7.3	6.6	5.9	5.3	4.7	4.1	3.6	3.2	2.8	2.5	2.2	1.9	1.6
-15	8.8	7.4	6.8	6.1	5.5	4.9	4.4	3.9	3.4	3.0	2.6	2.2	1.9	1.7	1.4	1.2
-20	7.5	6.3	5.7	5.1	4.6	4.1	3.6	3.2	2.8	2.4	2.1	1.8	1.5	1.3	1.1	0.94
-25	6.4	5.3	4.7	4.2	3.7	3.3	2.9	2.5	2.2	1.9	1.7	1.4	1.2	1.0	0.90	0.72
-30	5.5	4.5	4.0	3.6	3.2	2.8	2.4	2.1	1.8	1.5	1.3	1.1	0.96	0.80	0.67	0.56
-35	4.6	3.7	3.3	2.9	2.6	2.3	2.0	1.7	1.4	1.2	1.0	0.90	0.75	0.62	0.51	0.43
-40	4.0	3.2	2.8	2.5	2.2	1.9	1.6	1.4	1.2	1.0	0.86	0.73	0.62	0.51	0.41	0.33
-45	3.3	2.7	2.4	2.1	1.8	1.5	1.3	1.1	0.98	0.82	0.68	0.58	0.48	0.38	0.31	0.25
-50	2.8	2.3	2.0	1.7	1.5	1.3	1.1	0.93	0.78	0.66	0.56	0.47	0.38	0.31	0.25	0.20
-55	2.5	1.9	1.7	1.4	1.2	1.1	0.90	0.77	0.65	0.55	0.46	0.37	0.30	0.24	0.19	0.15
-60	2.1	1.6	1.4	1.2	1.0	0.87	0.74	0.62	0.52	0.43	0.36	0.30	0.24	0.19	0.14	0.10
-65	1.8	1.4	1.2	1.0	0.85	0.72	0.60	0.50	0.41	0.34	0.28	0.23	0.18	0.14	0.10	0.07
-70	1.5	1.1	0.99	0.84	0.71	0.60	0.50	0.42	0.36	0.30	0.25	0.20	0.15	0.11	0.08	0.05

We need to know the volumetric content of the different blending ingredients in the final product to calculate pour point of gasoil, as per below equation:

$(PP)_{blend} = \Sigma X_{vi} (PPBI)_i$, where:

X_{vi} = Volume Fraction

$(PP)_{blend}$ = Pour point blending index of the blend

$(PPBI)_i$ = Pour point blending index of component i, as taken from above table

The procedure normally used to calculate the pour point of the blended material can be summarized as follows:

1. Using as reference the pour point and the temperature that distillates the 50% (as per ASTM) of each blending stream, we retrieve the pour point blending indices for the different streams from the above table.
2. We multiply PPBI for individual distillates with their respective volume fraction to calculate the pour point factor of the blended gasoil.
3. We calculate the ASTM 50% distillation temperature (linearly additive) of the blend by multiplying the volume fraction with ASTM 50% temperature of each component and adding them together.
4. Using the blend ASTM 50% just calculated and the blending index for the blend from the pour factors (12.47) we interpolate the pour point of the blend from the table above.

(Petroleum Refining, by J. H. Gary, G. E. Handwerk, M. J. Kaiser, 5th Edition, CRC Press NY, 2007)

An alternative numerical method for calculating the pour point of blending stocks, which is easier to be used in resolving the blending problem through Excel Solver, is the following:

The pour point blending index is given by the below equations instead of aforementioned table:

In Kelvin:

$\mathrm{PPBI(K)}_i = 255.565 + 4.90211\mathrm{x}10^{-6} \exp [-0.016418\ (\mathrm{PPK}) - 0.0522346\ (\mathrm{T_bK}) +$

$+ 1.5751\ \mathrm{x}10^{-4}\ (\mathrm{PPK})(\mathrm{T_bK})]\ (\mathrm{PPK})^{1.67057}\ (\mathrm{T_bK})^{2.37162}$, where:

$\mathrm{PPBI(K)}_i$ = pour point blending index for component i in Kelvin
PPK = pour point in Kelvin
$\mathrm{T_bK}$ = ASTM distillation curve 50% temperature in Kelvin (≈average boiling point)

In Fahrenheit:
$\mathrm{PPBI(F)}_i = 0.1786 + 0.425117 \exp [0.0147\ (\mathrm{PPF}+70) - 0.00887\ (\mathrm{T_bF}) +$

$+ 4.925\ \mathrm{x}10^{-5}\ (\mathrm{PPF}+70)(\mathrm{T_bF})]\ (\mathrm{PPF}+70)^{0.1894}\ (\mathrm{T_bF})^{0.5855}$, where:

$PPBI(F)_i$ = pour point blending index for component i in °F
PPF = pour point in °F
T_bF = ASTM distillation curve 50% temperature in °F (≈average boiling point)

The procedure is to calculate the PPBI for each component using the equation then add to obtain the pour point of the blend: $PP = \Sigma X_{vi} PPBI(K)_i$

(https://www.e-education.psu.edu/fsc432/content/pour-point-blending)

Viscosity

Regarding determining the viscosity of a mixture (blend) of two or more components, two approaches will be presented that are commonly used in petroleum refining for predicting the viscosity of oil blends.

1st method is Gambill's, who proposed in 1959 the following equation for estimating the kinematic viscosity of a two liquid mixture: $v^{1/3} = x_a v_a^{1/3} + x_b v_b^{1/3}$

Where: v the kinematic viscosity and x the mass fraction of each component

2nd method Refutas (2000) proposed a method, where Viscosity Blending Number (VBN) is first calculated for each component and then it's used to determine the VBN of the mixture as shown below:

$$VBNi = 14.534 \, x \, ln(ln(vi + 0.8)) + 10.975$$

The VBN of the liquid mixture is then calculated, as follows:

$$VBNmixture = \sum_{i=0}^{N} xi * VBNi$$

The kinematic viscosity of the mixture can then be estimated using the VBN of the mixture, following the below equation:

$$vmixture = exp\,(exp(\frac{(VBNmixture - 10.975)}{14.534})) - 0.8$$

Chevron has developed an alternative formulation for calculating the VBN of the mixture, using volumetric fraction of each component υ_i as per below:

$$VBNi = \ln(vi))/\ \ln(1000 * vi)$$

$$VBNmixture = \sum_{i=0}^{N} vi * VBNi$$

The viscosity of mixture may then be calculated as described before (https://neutrium.net/fluid-flow/estimating-the-viscosity-of-mixtures).

Similar to pour point, the viscosity of blended oil products can also be calculated using respective blending index numbers, or plots developed for this purpose and can be found in bibliography (https://www.e-education.psu.edu/fsc432/content/pour-point-blending).

PRICES OF GASOIL BLENDING COMPONENTS

Now let’s see what prices should be used for structuring the objective (cost) function of our model. Likewise gasoline blending problem, the traders of the oil trading/refining company will advise the levels of each blending component and ready-to-sell product market value and their ongoing price fluctuation over the period of time we’re studying. The base prices that are published daily by Market Assessment Organizations like Argus or Platt’s, are commonly accepted as trading benchmarks for daily trading and agreement closures between trading and/or refining companies. On top of these assessments a premium or discount is determined to be added or subtracted from the base price of each blending component. Typical base prices along with their differentials are presented in the following table:

Table 18 Price allocation of blending streams

Stream	**Platt’s Assessment Reference**	**Base price $/mt**	**Differential $/mt**	**Total price $/mt**
HDT Diesel	Fob Med Ulsd10ppm	825,25	5,00	830,25
Kero Mild Hydro	Fob Med Jet	871,00	15,00	886,00
HDT FCC Naphtha	Fob Med Naphtha	590,50	10,00	600,50
HP-HCK Gasoil	Fob Med Gasoil	813,25	15,00	828,25

LP-HCK Gasoil	Fob Med Gasoil	813,25	5,00	818,25
HP-HCK Kero	Fob Med Jet	871,00	5,00	876,00

Once we have allocated a cost value to every blending stream expenditure and we determine the sale price of final grade (ULSD 10ppm) we follow the same optimization technique using MS Excel Solver add-in application to reach at an optimum solution by maximizing the sales revenue objective function or interchangeably minimizing the production cost objective function.

Needless to say that the rest of the constraints related to operation bottlenecks, i.e. storing capacity limitations, volume/mass availability of blending components etc. are being effected here as well and are part of the constraint listings that our variables should comply to. These constraints are also very dynamic, meaning that can be changed practically every day, this is why optimization is a very enhanced and detailed day-to-day business in the refining world.

INTRODUCTION

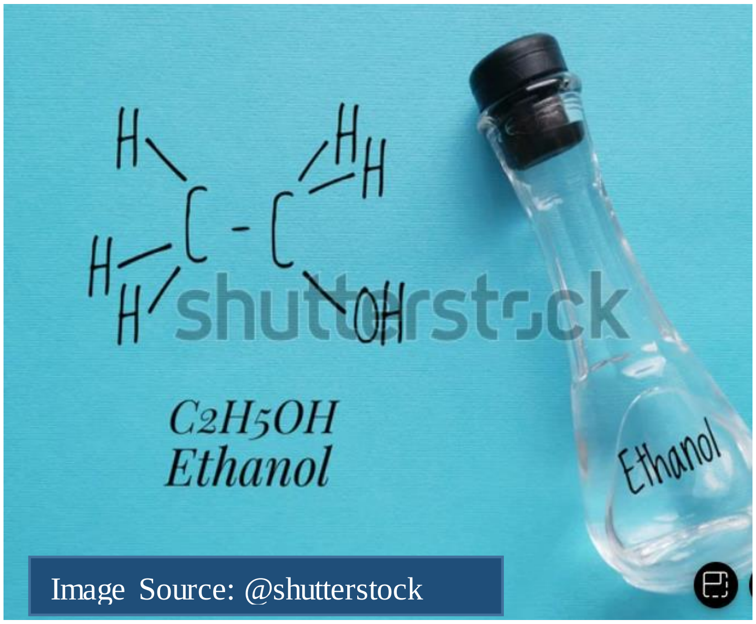


Image Source: @shutterstock

Ethanol has the chemical formula CH_3CH_2OH and is often simply called 'alcohol' by the general public. However, the term alcohol actually refers to a whole family of organic chemicals of which ethanol is only one member. Ethanol is also known by a number of other names such as ethyl alcohol, ethyl hydrate and grain alcohol. Alcohols have a hydroxyl group - that is an O to an H, in which an oxygen atom bonded to hydrogen is covalently bonded to a carbon. The hydroxyl group should not be confused with the hydroxide ion, OH- (https://www.chemistryworld.com/podcasts/ethanol/).

Ethanol or ethyl alcohol is a clear colourless liquid, it is biodegradable, low in toxicity and causes little environmental pollution if spilt. Ethanol burns to produce carbon dioxide and water. Ethanol is a high octane fuel and has replaced lead as an octane enhancer in petrol. By blending ethanol with gasoline we can also oxygenate the fuel mixture so it burns more completely and reduces polluting emissions. In Brazil 25% ethanol is mixed into petrol. In the United States two variants are available: (E85) containing 85% ethanol and 15% gasoline, but it cannot be used widely – only to modified engines and the most common blend which is 10% ethanol and 90% petrol (E10). Vehicle engines require no modifications to run on E10 and vehicle warranties are also unaffected (https://www.eubia.org/cms/wiki-biomass/biofuels/bioethanol).

In 4000 BC humans used to make alcohol as a beverage from cereals, berries, grapes using fermentation. Since antiquity, olive oil and other oils derived from plants and animals have been used for lamp oil. In early 1700s lamps were operated with burning vegetable oil and fats and in 1800s whale oil was preferred until a modern method of refining kerosene was made up by Abraham Gesner (1846). By late 1830s due to the diminishing supply of expensive whale oil, ethanol blended with turpentine was established as a fine substitute. Before the discovery of petroleum by Edwin Drake in 1859, ethanol was developed as an alternative fuel. To fund the Civil War, a $2.08 tax per gallon of ethanol was imposed by the US Congress in 1862. This tax made ethanol more expensive than gasoline, favoring gasoline's use in the internal combustion engines. Even after the tax's repeal (1906), it was extremely difficult for ethanol to compete with gasoline infrastructure.

Henry Ford, the famous American industrialist, constructed ethanol-powered tractors and in 1906 he said that carburetors on his model T cars will use gasoline and ethanol alike. In 1925, Ford named ethyl alcohol as the "fuel of the future" and Alexander Graham Bell stated in a 1917 National Geographic interview that "Alcohol makes a beautiful, clean and efficient fuel that can be produced from any vegetable matter, capable of fermentation, such as crop residues, grasses, farm waste and city garbage".

During the 1920s and 1930s, Ford promoted a new movement called chemurgy. Chemurgy spotted biobased materials for crop utilization, under the scope of producing synthetic rubber, during the onset of World War II. In 1943, ethanol was used to produce the 77% of the synthetic rubber in the States. During world war years, where rationing the raw materials and natural resources was really important, ethanol employed as a gasoline substitute. To counter the rapid increase in oil prices, which has continued through the early twenty-first century, Arab oil embargoes for the 1970s remembered by those whose experienced it, as a first vocal call for domestic source of renewable fuels. In 1979, the first pilot bioethanol plant was established at South Dakota University (Songstad et al., 2009). Needless to say that in 1973, due to OPEC oil export embargo and in 1979, during the Iranian revolution, the significant oil supply shortfalls and the soaring price of crude oil affected severely the economies of the major industrial countries, including the US, Western Europe, Japan, Canada and Australia.

The expansion of usage of renewable fuels, like ethanol, have fanatic supporters and persistent opponents alike. The expansion of biofuel crops by clearing land for planting biofuel crops can harm the environment by displacing other crops. It might also threaten biodiversity and wildlife in terms of conversion of natural forests and grassland into new cropland for growing feedstock meant for biofuels production. Biofuels enemies, to the right to human's food, frequently claim that "biofuels embracement is a crime against humanity to divert arable land to the production of crops which are then burned for fuels. In Indonesia and Malaysia, for the oil plant plantation development, around 14-15 million hectares of peatlands have been cleared. Water pollution and air pollution caused by production and combustion of corn-based ethanol might harm intensely human health and the environment. Shifting of biodiverse ecosystem to industrial monocultures might ultimately pose a threat to ecosystem integrity (Hoekman, 2009 & Pimentel et al., 2009).

METHODS OF PRODUCTION

Commercially is produced mostly from starch-/sugar- based crops, like sugarcane, sugar beet – it's a plant whose roots contain high concentration of sucrose and it is getting grown commercially for sugar production – and corn and other sources, like cassava or cellulosic materials (e.g. grasses, trees, waste-product from crops). In European countries, the predominant feedstock is wheat and sugar beet, whereas in Brazil the primary feedstock is sugarcane.

Sugar beet root, image source: @shuttetstock

Cassava root, image source: @shutterstock

Selecting the feedstock depends on how difficult is to grow a specific ethanol oriented crop, where crops can be cultivated geographically and how far the cultivations are located from the storage and treatment plant facilities and whether the crops are being isolated from other uses, such as livestock feed or human nutrition. Crop residues and wood wastes can also be used as feedstock. Bioethanol is mainly produced by the plant contained sugar fermentation process, called “biochemical conversion”, but plant material can be converted to ethanol using heat and chemicals in a process called “thermochemical conversion” (https://afdc.energy.gov/fuels/ethanol_production.html).

STARCH- AND SUGAR- BASED ETHANOL PRODUCTION

US produce ethanol that they need from starch-based crops by dry or wet-mill processing. In dry-mills grinding corn into flour occurs and then flour is fermented into ethanol with co-products of distillers grains and carbon dioxide. In wet-mills corn sweeteners are produced, along with ethanol and other co-products, such as corn oil and starch. Wet-mills separate starch, protein and fiber in corn before processing these components to products, like ethanol.

The dominant technology for producing bioethanol is fermentation followed by distillation. In the first stage (fermentation) the biomass is decomposed using bacteria and enzymes. This biochemical conversion is still based on Baker’s yeast (Saccharomyces cerevisiae) which requires monomeric sugars as raw material.

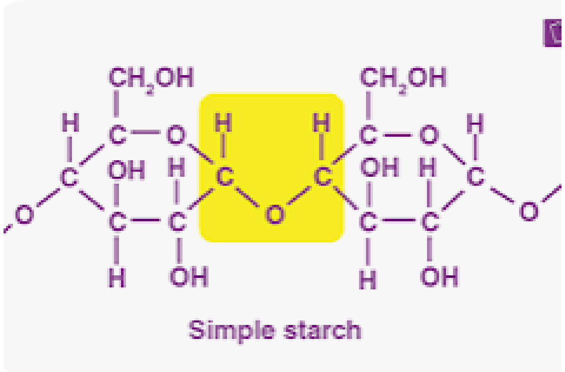


Figure 19 Simple starch chemical type

Figure 19 Simple starch chemical type

Yeast fermentation produces 0,51kg of ethanol from 1 kg of any C6 sugars glucose, mannose and sucrose. On the other hand starch and lignocellulose feedstocks are containing poly-sugars and hydrolysis technique is required to brake the bonds between monomers and produce simple C6 sugars for fermentation. First the grain need to be grinded and milled to release its starch. Then the material is diluted with water to adjust the amount of sugar in the mash. This enables the activation of the yeast and makes mash easier to stir and handle. The mixture is cooked to dissolve the water-soluble starches. The starch is converted to sugars at the same time. This process is effected either by using enzymes or by acid hydrolysis. In latter case, dilute mineral acid is added to the grain slurry prior cooking. The result of these processing steps is short carbohydrates to be formed and to be fermented easily by micro-organisms. For growing the yeast the slurry must be slightly acid, pH between 4,8-5,0. During fermentation a mixture of ethanol and water is produced. In addition CO_2 is generated as a by-product. Taking the mixture beyond its azeotropic equilibrium, through a series of distillation and dehydration processes, to produce anhydrous ethanol, so called bio-ethanol, is the final stage.

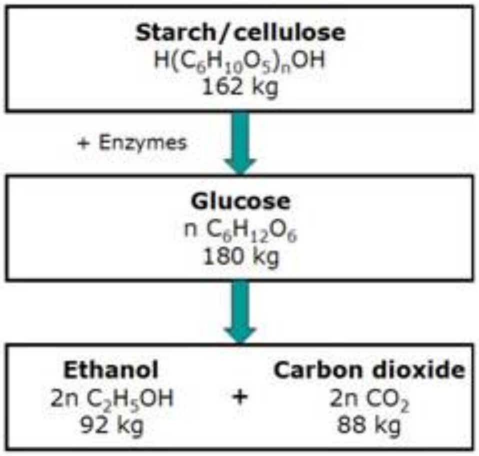


Figure 20 C6 Sugars produce Ethanol & CO_2

Figure 20 C6 Sugars produce Ethanol & CO_2

ETHANOL PRODUCTION IN BRAZIL

The production of ethanol is considerably simpler in Brazil as there is no starch to process. The sugarcane is harvested and milled to extract sugar (sucrose) and the rest of the plant, known as 'bagasse', is retained as it can be burnt in boilers. The sugar can be processed to produce sugar and the residue and molasses used for fermentation or the sugar juice used directly (Figure 22). The sugar and salts are run into 100,000–400,000 l open bioreactors and inoculated with yeast. After fermentation has ceased, the yeast is removed by flocculation or centrifugation and the liquid distilled. If more than 95.6% ethanol is required a second distillation is carried out with the ethanol blended with fossil oil. The residue from the first distillation can be used as a fertilizer. The economy of the process is improved greatly as the residue from the sugarcane (bagasse) is used to fire boilers which supply steam for the distillation process (Scragg A.H., 2009, Biofuels production, application and development, CABI).

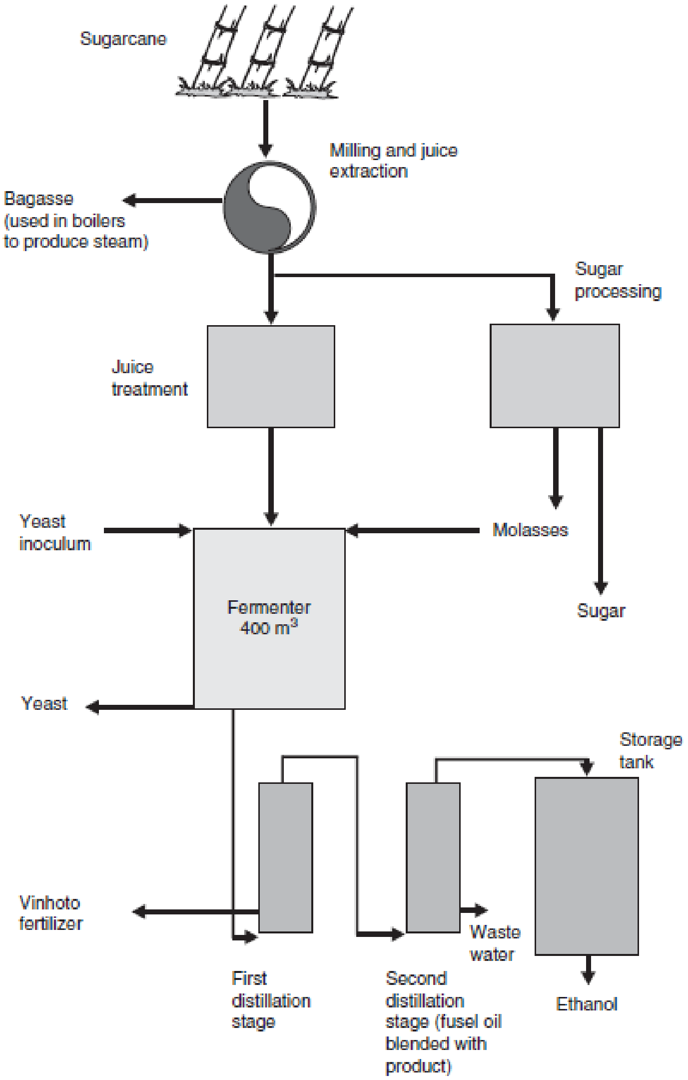


Figure 21 Ethanol production process through sugarcane treatment

CELLULOSIC PRODUCTION

In the case of treatment lignocellulosic biomass – such as grass, wood, crop residues - to produce ethanol the above process is primarily being followed but it’s more complicated. It involves four major steps, pretreatment of biomass, hydrolysis of the pretreated biomass to brake cellulose into sugars, followed by fermentation of released sugars and ethanol separation at the final stage.

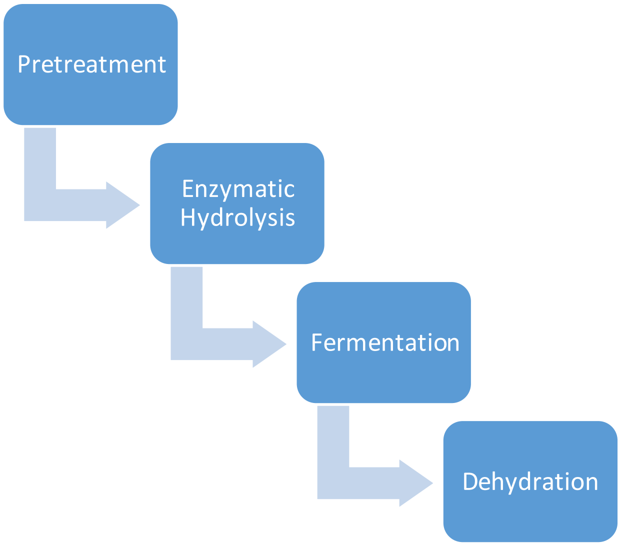


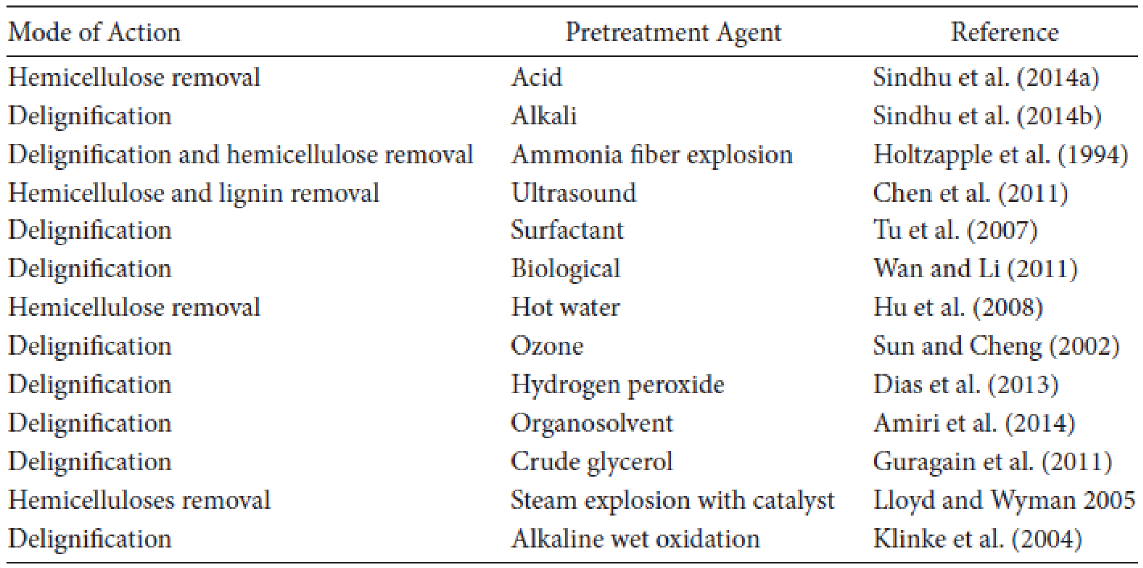
Figure 22 Processing Steps of cellulosic origin ethanol production

PRETREATMENT

Pretreatment is the first step in bioethanol production and it's essential for successful downstream operation. It alters biomass macroscopic and microscopic structure so that hydrolysis of carbohydrate to monomeric sugars take place rapidly with better yields. It makes up for more than 40% of the total processing cost. Conventional techniques are removing either lignin of hemicellulose from biomass structure, decompacting it and making it more accessible to enzyme attack. The most widely used technique include acid hydrolysis, dilute acid treatment, hot water and lime. This method has been extensively studies and commercialized. One of the major advantage is the generation of a separate pentose and hexose stream. Dilute acid treatments are always accompanied by formation of inhibitors, like furfural, hydroxymethylfurfural, phenolics and organic acids.

Other pretreatment methods currently employed include physical, chemical and biological pretreatments and are reviewed in the following table:

Table 19 Pre-treatment Techniques and Agents



Mode of Action	Pretreatment Agent	Reference
Hemicellulose removal	Acid	Sindhu et al. (2014a)
Delignification	Alkali	Sindhu et al. (2014b)
Delignification and hemicellulose removal	Ammonia fiber explosion	Holtzapple et al. (1994)
Hemicellulose and lignin removal	Ultrasound	Chen et al. (2011)
Delignification	Surfactant	Tu et al. (2007)
Delignification	Biological	Wan and Li (2011)
Hemicellulose removal	Hot water	Hu et al. (2008)
Delignification	Ozone	Sun and Cheng (2002)
Delignification	Hydrogen peroxide	Dias et al. (2013)
Delignification	Organosolvent	Amiri et al. (2014)
Delignification	Crude glycerol	Guragain et al. (2011)
Hemicelluloses removal	Steam explosion with catalyst	Lloyd and Wyman 2005
Delignification	Alkaline wet oxidation	Klinke et al. (2004)

ENZYMATIC HYDROLYSIS

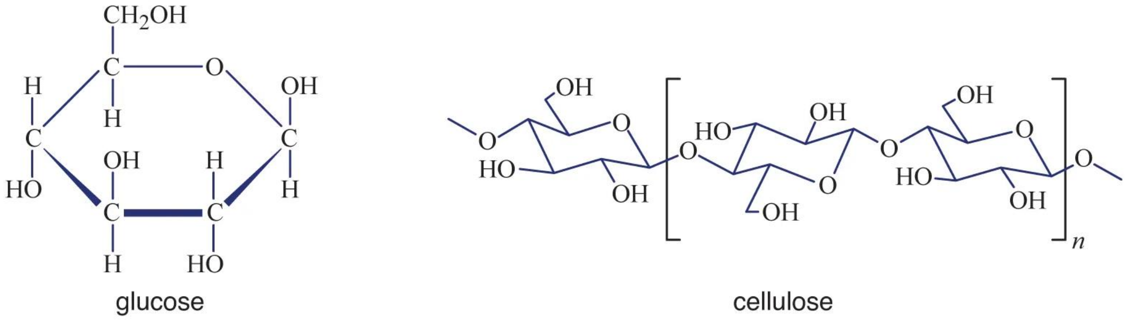
The major factor that limits bioethanol production from lignocellulosic biomass the high cost and the hydrolytic efficiency of the enzymes. The success of this step relies heavily on the effectiveness of pretreatment stage, as hydrolysis rate gets improved with increase in porosity of the substrate and cellulose accessibility to cellulases. Accessory enzymes are those enzymes that act on less abundant linkages found in plant cell walls. These include arabinases, lyases, pectinases, galactanases, and several types of esterases. Process' efficiency can be improved by supplementing the accessory enzymes. Enhancements on hydrolysis kinetics can help in designing and operating the hydrolysis reactors, improving in turn the economic viability of the entire process.

One of the most efficient cellulose-producing fungi is Trichoderma reesei. The conversion of cellulose to glucose monomers takes place with the help of the combined action of three enzymes—endoglucanase, exoglucanase, and β-glucosidase. Endoglucanases hydrolyze β-1,4 glycosidic linkages in the cellulose chain; cellobiohydrolase cleaves off cellobiose units from the end of the chain, and β-glucosidase converts cellobiose to glucose (Himmel et al. 1996). Phenolic compounds derived from lignin are known to inhibit cellulases. Another drawback of lignin is that it causes nonproductive adsorption that limits the accessibility of cellulose to cellulases.

FERMENTATION

Sugars are fermented into ethanol and lignin is recovered and used to produce energy to power the process. The thermochemical conversion process involves adding heat and chemicals to a biomass feedstock to produce syngas, which is a mixture of carbon monoxide and hydrogen. Syngas is mixed with a catalyst and reformed into ethanol and other liquid co-products.

Lignocellulosic biomass contains carbohydrate polymers called cellulose (40-60% of dry weight) and hemicellulose (20-40% of dry weight) that can be converted to sugars. Cellulose is composed of glucose molecules bonded together in long chains that form a crystalline structure. Hemicellulose consists of a mixture of polymers made up from xylose, mannose, galactose, or arabinose. It is much less stable than cellulose. Both materials are not soluble in water. The remaining fraction, a complex aromatic polymer called lignin (10-25% of dry weight) cannot be fermented because it is resistant to biological degradation. This material can be utilized for the production of electricity and heat (https://www.eubia.org/cms/wiki-biomass/biofuels/bioethanol).



glucose

cellulose

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Figure 23 The molecules of glucose and cellulose

We could schematically present ethanol production from lignocellulose in figure 25. It consists of a physically separated process of pretreatment, followed by the process of hydrolysis with the addition of suitable enzymes and the fermentation process. Production sequence is combined with on-site cultivation of filamentous fungi for production of cellulolytic enzymes and on-site propagation of engineered pentose-fermenting yeast strains (Michel Jansel, Jasmine Melanie Bracher, Ioannis Papapetridis et al. Saccharomyces cerevisiae strains for second-generation ethanol production: from academic exploration to industrial implementation).

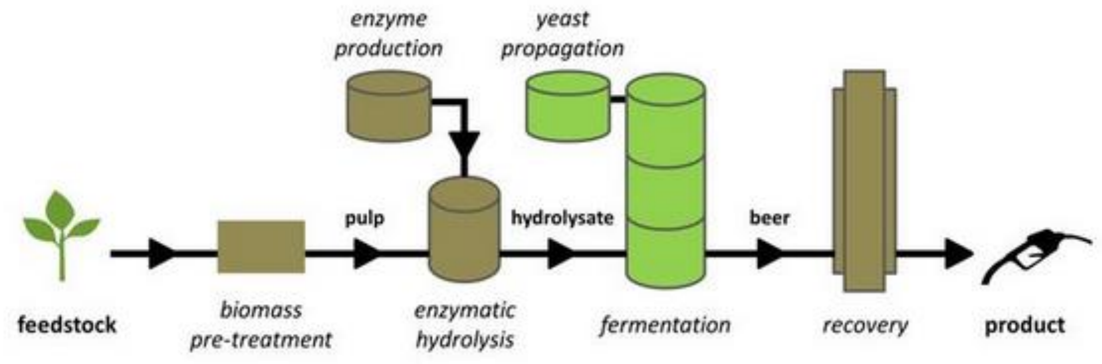

Figure 24 Review of production from cellulose feedstock

DEHYDRATION

To be used as a fuel, ethanol purity needs to be almost 100%. This means that the water content must be much lower compared to ethanol produced by current industrial technology. The product of fermentation needs to be upgraded to about 95% purity, which is known as rectified spirit. The residue of fermentation is composed of residual lignin, unhydrolyzed cellulose and hemicelluloses, ash, enzyme, organisms and other components. This residue can be concentrated and burnt for power generation. Distillation or distillation combined with absorption methods are extensively used for ethanol dehydration. The remaining water cannot be removed by distillation, since ethanol forms a constant boiling mixture with water known as azeotrope. In small scale applications we can add some dehydrants like lime that are capable of separating water from ethanol. In industry several technologies are available, such as the use of molecular sieves and membrane separation.

WHERE BIOETHANOL IS BEING PRODUCED

We've seen how ethanol is produced, time to see where it's being produced. As mentioned before and as below graph verifies, the predominant countries-producers are US with around 15 bil gallons per year and Brazil with 8 bil gallons per year (1 gallon (US) = 3.78 liters). These two accumulate the 80% and more of the global production (Alternative Fuels Data Center/US Department of Energy).

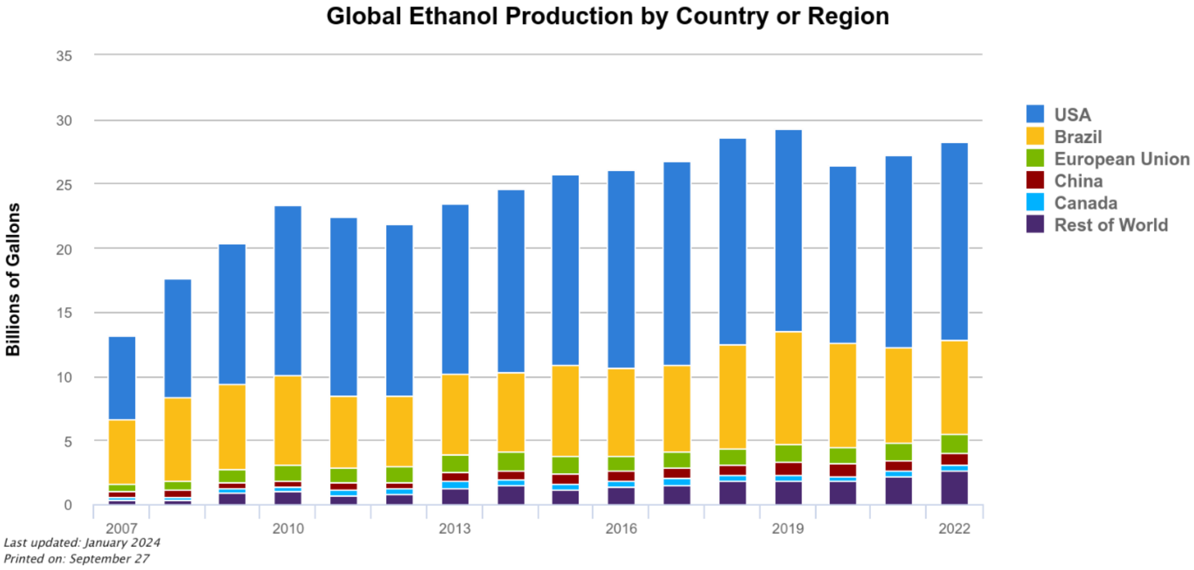

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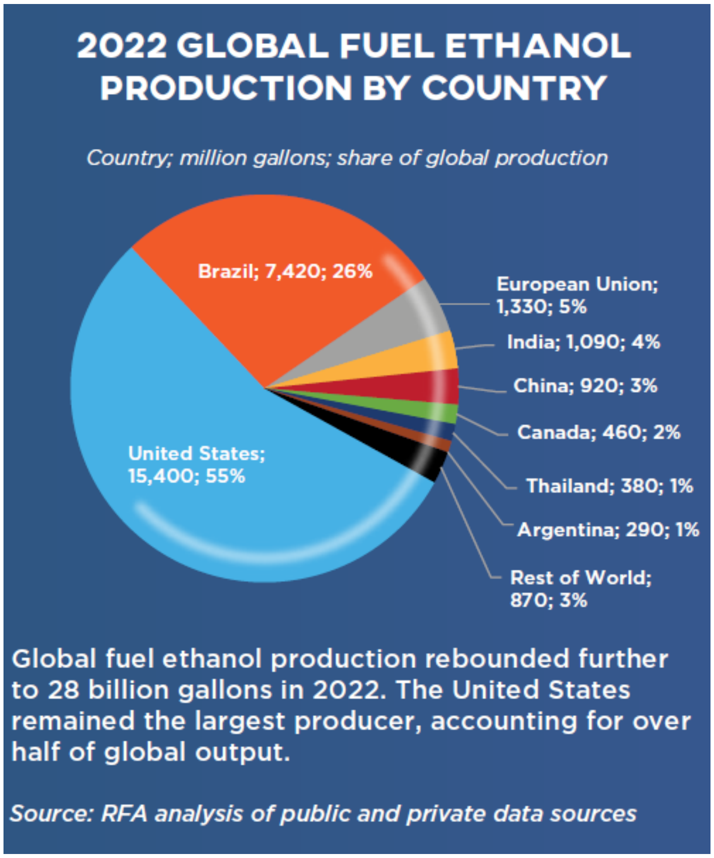
Figure 25 Ethanol Production by Region

Whereas, in 1980 in US a handful of ethanol plants produced 175 million gallons of renewable fuel, in 2022 more than 200 bio-refineries across the country, produced over 15.4 billion gallons of ethanol. Nearly every gallon of gasoline sold in the US market contains at least 10% ethanol and US Environmental Protection Agency (EPA) has already approved the E15 blend, which contains 15% ethanol, for more than 97% of the existing US auto fleet (Renewable Fuels Association Outlook).

We can see in more detail the 2022 global fuel ethanol production by country in the following pie chart with data used and analyzed by 2023 Renewable Fuels Association (RFA) Outlook.

Because US is the “big player” of the game they export to the whole world and especially to Canada, South Korea and European Union (EU) nearly 1.5 bil gallons per year. In figure 31, data retrieved by the same source, the percentages of US ethanol exports to the different country-consumers are illustrated (US Dept. of Commerce, US Census Bureau, Foreign Trade Statistics).


2022 GLOBAL FUEL ETHANOL PRODUCTION BY COUNTRY

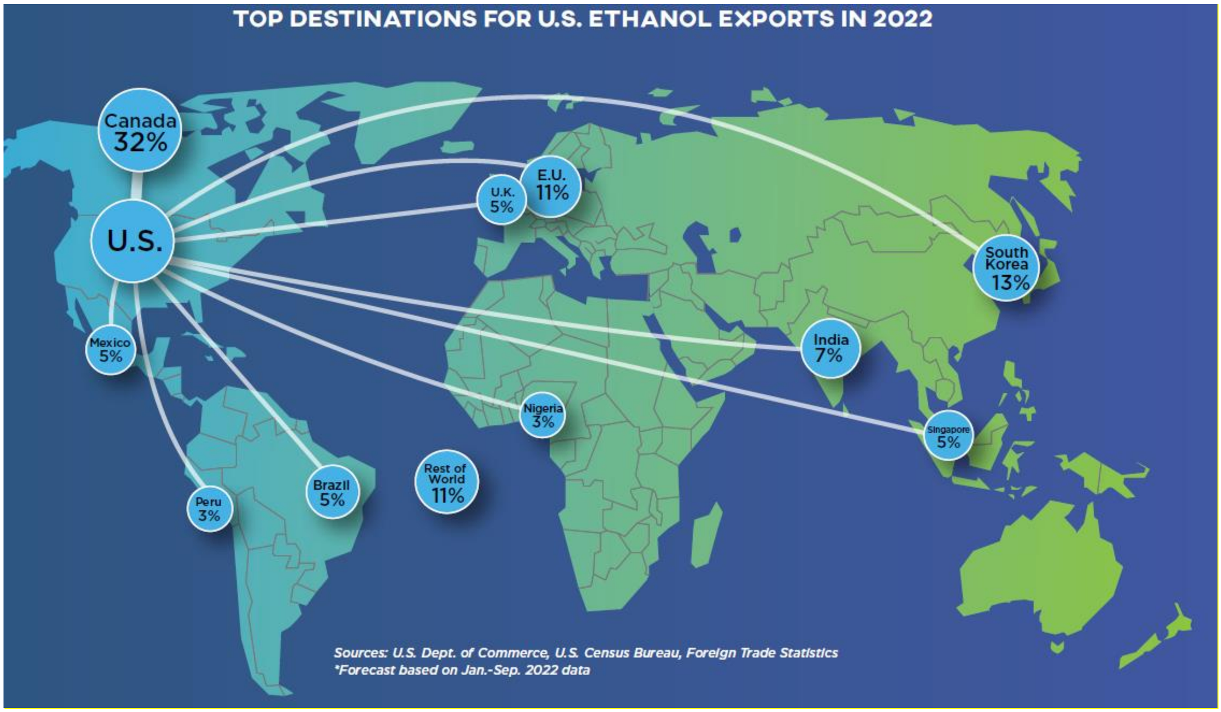
Country; million gallons; share of global production

Global fuel ethanol production rebounded further to 28 billion gallons in 2022. The United States remained the largest producer, accounting for over half of global output.

Source: RFA analysis of public and private data sources

Figure 26 Ethanol production by country - RFA data

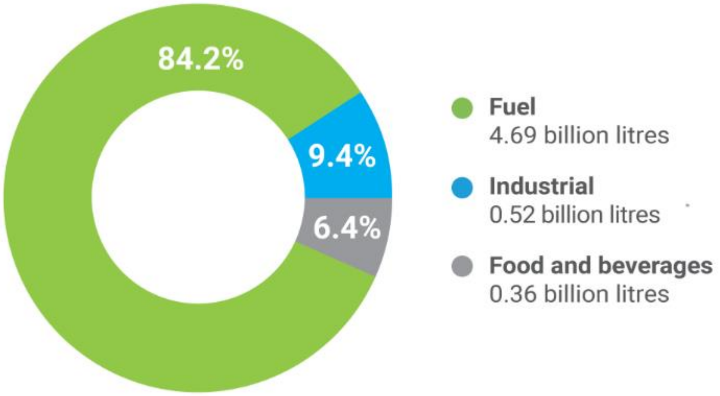
Figure 26 Ethanol production by country - RFA data


TOP DESTINATIONS FOR U.S. ETHANOL EXPORTS IN 2022

Sources: U.S. Dept. of Commerce, U.S. Census Bureau, Foreign Trade Statistics
*Forecast based on Jan.-Sep. 2022 data

Figure 27 USA exports ethanol to the world – US Dept. of Commerce data

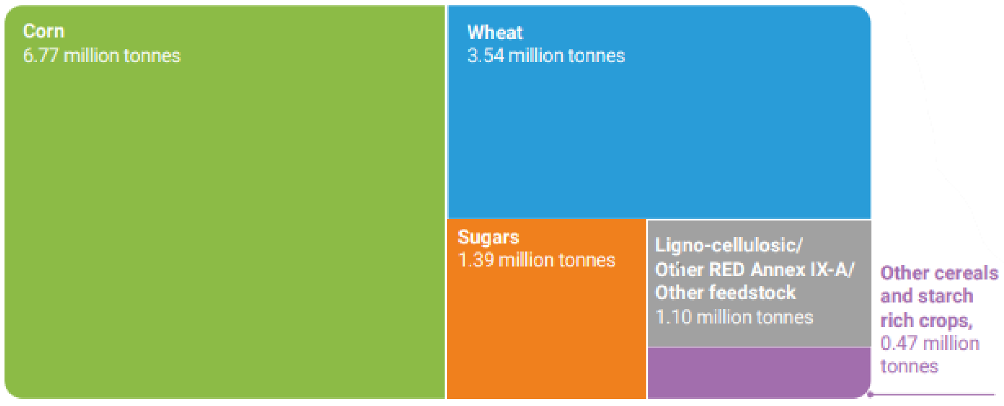
On the other hand, European Union, as we can notice from figure 30 (pie chart), produces only 5% of the global production, i.e. 1.3 bil gallons of ethanol but it's not adequate for EU countries' needs. In 2021, EU based industries produced 5.58 bil liters of ethanol with fuel accounted for 84.2%, industrial applications 9.4% and food and beverages sector 6.4% (fig. 32 – source: ePURE).



Aggregated and audited data of ePURE members. Ethanol volumes in pure alcohol

Figure 28 Ethanol production targeted by sector in EU

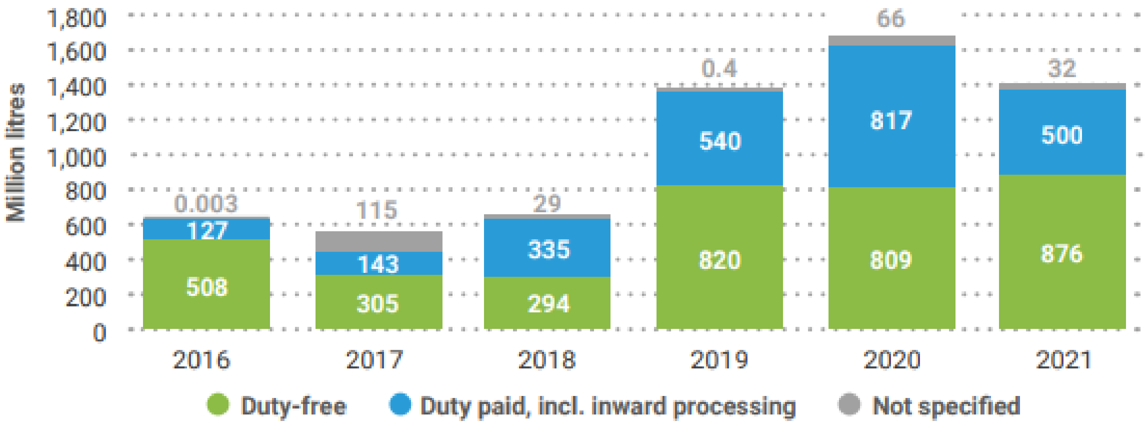
In the EU, bioethanol is produced primarily from corn and wheat, at percentages of 50.4% and 21.8% respectively and secondary from sugars (14.5%) and other cereals and starch rich crops (3%) (fig. 33 – source: ePURE).



Source: *Aggregated and audited data of ePURE members. Sugars – sugar equivalent;*

Figure 29 Source of ethanol production in EU

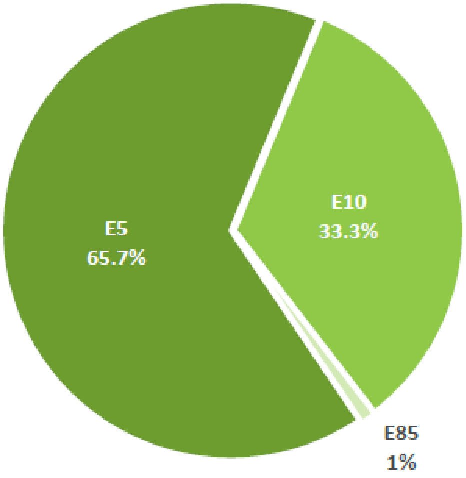
Despite this production capacity, in 2021 European Union imported 1.4 bil liters of product to meet its demand; mainly from US, Peru, Pakistan and Brazil (fig. 34 - source: Eurostat).



Source: Eurostat, EU28 imports until 2019, EU27 imports without the UK as of 2020

Figure 30 EU ethanol imports by region per annum

The dominant fuel in petrol engines consumed in EU countries is E5, meaning a blend of 5% ethanol mixed to 95% with fossil gasoline. As per European Environment Agency (EEA) data of 2021, E5 represents the bulk of the EU-27 petrol market. However, the E10 (i.e. 10% ethanol mixed to 90% gasoline) market share has been steadily increasing in the recent years. E10 represents the one third of the market whilst E0 is almost completely phased out, with a remaining share of just 0.3%.



E10 is currently available in 15 EU Member States, as well as the UK: Belgium, Bulgaria, Denmark, Germany, Estonia, Finland, France, Latvia, Lithuania, Luxembourg, Hungary, the Netherlands, Romania, Slovakia and Sweden.

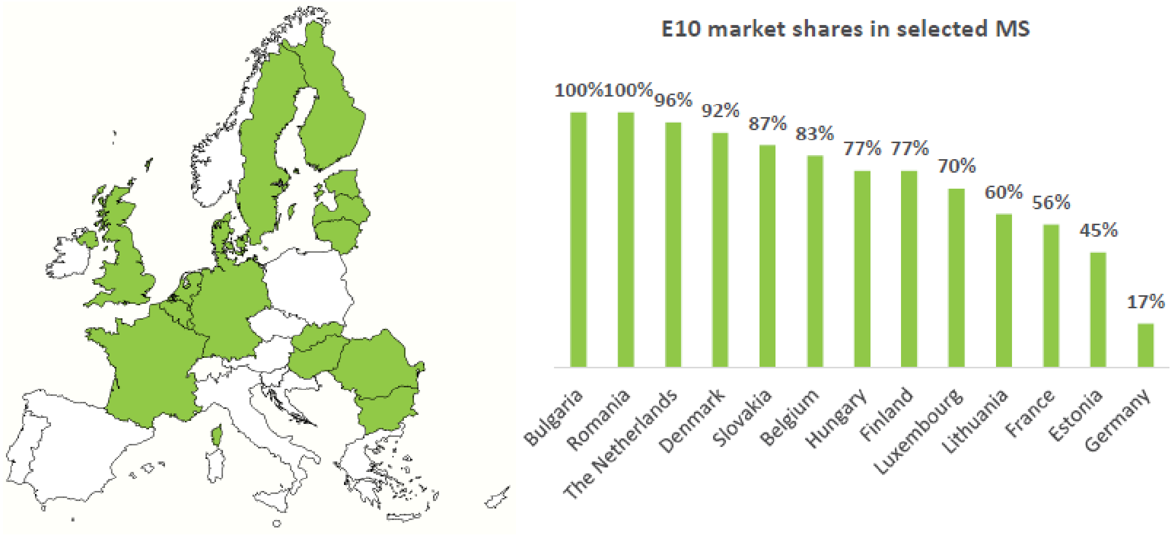


Figure 31 E10 market share in Member States

Bioethanol consumption in Europe increased slightly till the COVID-19 years and has soared just after, reaching the 6.33 million cubic metres in 2023. At the same time imports have been quadrupled compared to 2016 figures.

Table 20 Bioethanol Market (related to fuels) in Europe (in million cubic metres)

YEAR	**2015**	**2016**	**2017**	**2018**	**2019**	**2020**	**2021**	**2022**	**2023**
CONSUMPTION	4.53	4.43	4.68	5.01	5.22	5.16	5.84	6.20	6.33
IMPORTS	0.29	0.31	0.11	0.19	0.67	0.83	0.48	1.26	1.39
EXPORTS	0.52	0.57	0.19	0.19	0.65	0.65	0.26	0.49	0.62

Source: US Dept. of Agriculture, Foreign Agricultural Service (European Union: Biofuels Annual)

The principal consumer of ethanol in EU-27 community during 2023 (and previous years) was France and Germany with about 1.5 million cubic metres consumption each. These countries jointly cover almost half of the total EU-27 annual consumption. The following consumer countries (Netherlands and Poland) accumulate about one third of Germany's needs, as clearly stated in the following graph:

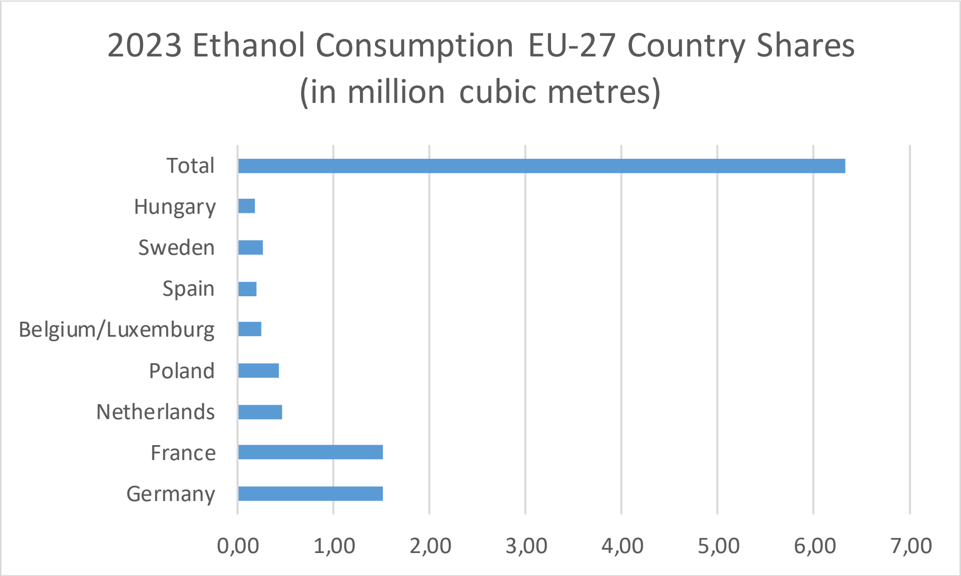


Figure 32 Ethanol Consumption in EU-27 – 2023 data

In 2021, the biogasoline incorporation rate across the EU-27 was 4.6% in energy terms, and 6.8% in volume, as per 2023 Eurostat's data. The corresponding quantity of biogasoline, including renewable methanol, ethanol, ETBE, or MTBE, was 3,023 ktoe. Biogasoline consumption in the EU reached historic highs after a decrease in 2020 during the COVID-19 crisis.

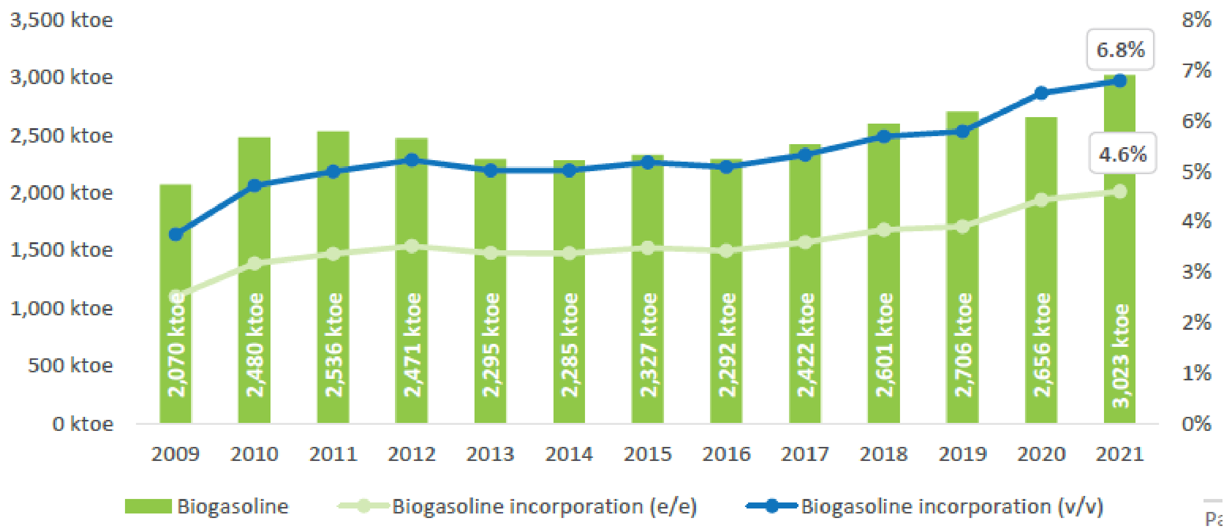


Figure 33 Biogasoline penetration in EU countries – Eurostat data

In the US a rapid soar of ethanol consumption was reported in the years after 2000 and from 2010 onwards, respective figures are steadily over 20 mil barrels per year, even exceeding the 30 mil barrels per year in the recent years. As anticipated the consumption trend is strongly related to legislation. The U.S Environmental Protection Agency's policy towards the leaded gasoline phase-out in the 1980s, caused an increase of ethanol usage as an octane booster and volume extender. Nonetheless, MTBE, (Methyl Tert-Butyl Ether) was the dominant ingredient in most oxygenated gasoline markets (1990s), until the increasing restrictions on MTBE blending came into force, effecting to a rapid growth in US ethanol production since 2002, as it's also highlighted in the following graph:

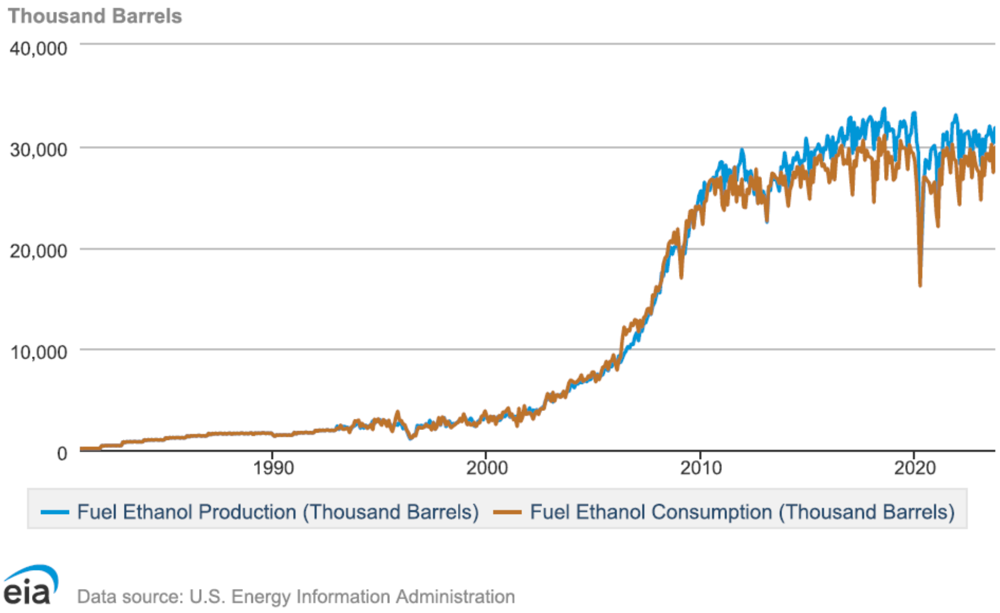


Figure 34 Ethanol Production/Consumption in US - EIA data

It's really important to keep in mind that corn origin ethanol reduces carbon emissions by nearly 50% on average compared to gasoline. In the US, transportation sector is largely responsible for the GHG emissions, accounting for 33% of the economy-wide total in 2019. Although the transport emissions declined by 6% between 2005 and 2019, the majority of reduction came from light duty vehicles. On the contrary, within the same time period the emissions from freight vehicles rose by 5% and from aviation segment rose by 14%.

In US, Renewable Fuels Association's (RFA's) members are committed to achieve an average carbon reduction of 70% compared to gasoline by 2030. RFA has released a report titled "Pathways to Net-Zero Ethanol: Scenarios for Ethanol Producers to Achieve Carbon Neutrality by 2050". This "Pathway" identifies five core actions need to take effect for reaching the aforesaid goal. Those are the following:

- Renewable energy use by corn and ethanol producers
- Expanded adoption of corn kernel fiber fermentation at dry mills
- R&D investments in ethanol production techniques to improve efficiency and yields
- Carbon capture and sequestration by ethanol facilities
- Expansion of conservation tillage and other low-carbon practices by corn growers

Carbon capture and sequestration and expanded renewable energy are already in extensively use at farms and bio-refineries.

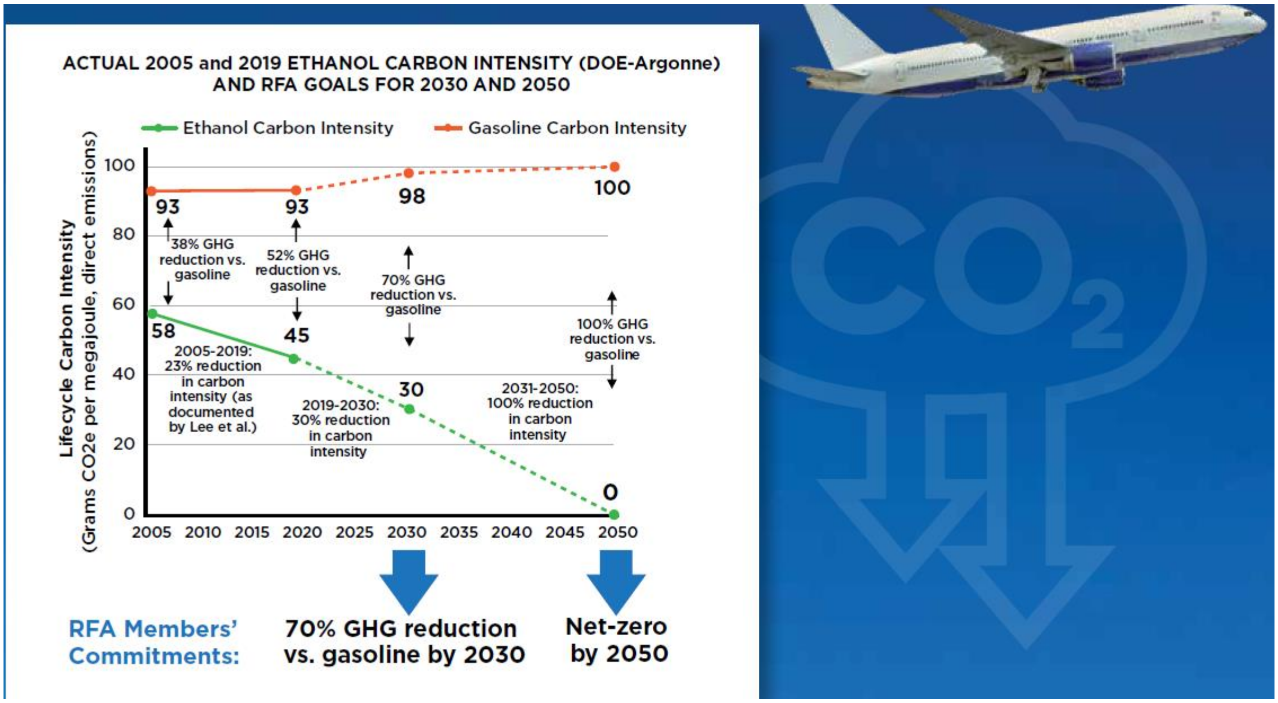


Figure 35 RFA Member's commitments on GHGs reduction

Several American institutions and organizations have conducted surveys to determine the path that US need to follow to reach the "NET-ZERO" goal by 2050. Under current policy, passenger vehicle emissions are projected to be 20% lower in 2030 compared to 2019, primarily due to electrification evolution. However, the same progress is not projected for freight transportation and air travel. Freight emissions are projected to decline by 9% and aviation emissions are expected to increase by 1% by 2030 (see figure 35) (Rhodium Group: Closing the Transportation Emissions Gap with Clean fuels, by Emily Wimberger, Trevor Houser and John Larsen).

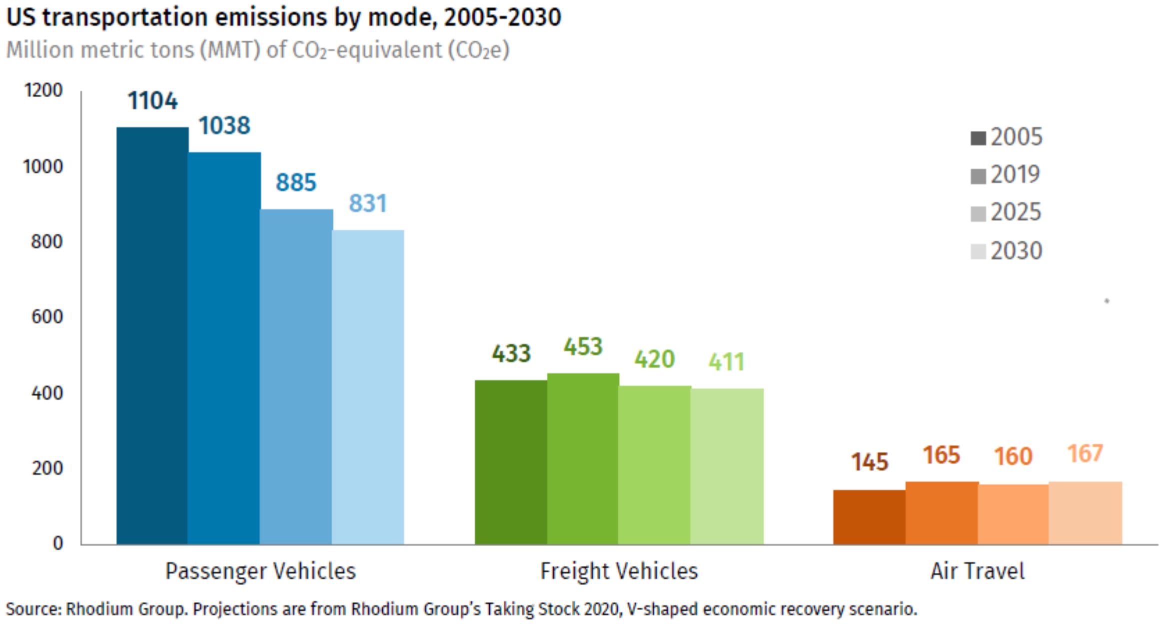


Figure 36 Transportation emissions reduction in US- Rhodium Group data

Institutions coping with the forecasting of CO_2 emissions are using different scenarios to found their analysis. Under the scenario of modest electrification of Light-Duty Vehicles (LDVs) - reaching the lower end of aggressive projections, i.e. 35% of sales in 2030 and 77% in 2040 - it's forecasted that emissions will remain over 700 mil Metric Tons in 2050. These CO_2 quantities need to be displaced through mobility strategies that reduce vehicle usage and increase use of mass transportation facilities. Under the scenario of increased LDVs electrification - more than half sales nationally will be electric by 2030 and nearly 90% by 2035 – 520 mil Metric Tons emissions (35% of the current levels) will remain in the transportation sector in 2050.

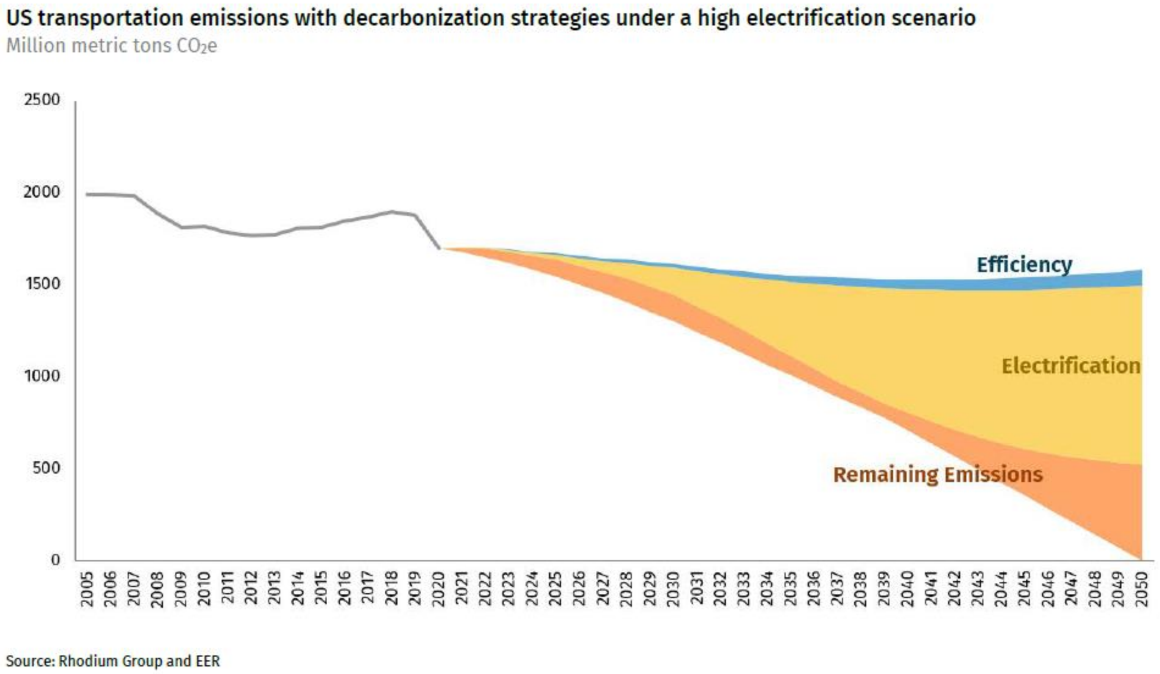


Figure 37 Transportation Emissions reduction – High electrification scenario

That means that electric vehicles alone cannot solve the problem of emissions and meet the goal of net-zero emissions in the transportation sector by 2050. Federal Government needs to deploy a portfolio of clean fuels, i.e. a combination of biofuels, electro fuels (e-fuels) and carbon-neutral fossil fuels. Following this path the transportation emission gap can be closed.

Clean Fuels Portfolio

Biofuels	Conventional and advanced fuels made from biomass feedstock
Electro fuels – e-fuels	Drop-in liquid replacement fuels made from electricity, carbon and hydrogen
Carbon-neutral fossil fuels	Petroleum fuels whose emissions are offset with negative emissions technology

The optimum portfolio will depend upon technology cost, feedstock availability and regionally studied air-quality issues. In addition, high-quality wind potential, solar resources availability and characteristics of the local agricultural economy will diversify the mixture of above elements (Rhodium Group, Closing the Transportation Emissions Gap with Clean fuels, by Emily Wimberger, Trevor Houser and John Larsen).

Bioethanol has an energy content of 23.5 MJ/l and therefore contains 32.5% lower energy content than gasoline, i.e. about two-third of the energy content of the latter on a volume base. This means that, for mobility applications, for a given tank volume, the range of the vehicle is reduced in the same proportion.

The octane number of ethanol is higher than that for petrol, therefore ethanol has better antiknock characteristics. This better quality of the fuel can be exploited if the compression ratio of the engine is adjusted accordingly. This increases the fuel efficiency of the engine. The oxygen content of ethanol also leads to a higher efficiency, which results in a cleaner combustion process at relatively low temperatures.

The Reid Vapour Pressure, a measure for the volatility of a fuel, is very low for ethanol. This indicates a slow evaporation, which has the advantage that the concentration of evaporative emissions in the air remains relatively low. This reduces the risk of explosions. However, the low vapour pressure of ethanol, together with its single boiling point, is disadvantageous with regard to engine start at low ambient temperatures. Without aids, engines using ethanol cannot be started at temperatures below 20ºC. Cold start difficulties are the most important problem with regard to the application of alcohols as automotive fuels.

Table 21 Basic attributes comparison between Gasoline, Bioethanol & ETBE

Property	Gasoline	Bioethanol	ETBE
Molecular weight [kg/kmol]	111	46	102
Density [kg/l] at 15ºC	0.75	0.80-0.82	0.74
Oxygen content [% wt]		34.8	
Lower Calorific Value [MJ/kg] at 15ºC	41.3	26.4	36
Lower Calorific Value [MJ/l] at 15ºC	31	23.5	26.7
Octane number (RON)	97	109	118
Octane number (MON)	86	92	105
Cetane number	8	11	-
Stoichiometric air/fuel ratio [kg air/kg fuel]	14.7	9.0	-
Boiling temperature [ºC]	30-190	78	72
Reid Vapour Pressure [kPa] at 15ºC	60-80	16.5	28

Ethanol integration for transportation purposes has reduced the CO_2 emissions in U.S. by 50%. In particular, in 2021, 54,5 million metric tons of emissions were saved thanks to ethanol, equivalent to erasing 12 million passenger cars out of the roads for one year. Under that perspective many voices are backing the wider use of ethanol not only in road transportation segment but also in other fields, like aviation industry. In this debate, one of the largest biofuels production associations in the States, Growth Energy, has urged the U.S. Internal Revenue Service to include largely ethanol industry in its effort to reach Federal Government Administration's goals to expand the use of Sustainable Aviation Fuel (SAF). Particularly, Federal policies pledge to reach 3 billion gallons of SAF production per year by 2030 and 35 billion gallons per year by 2050. Ethanol, which accounts for 80% of the biofuels production capacity in the country, can be utilized in the aviation sector, if proper economic conditions are in place and if lifecycle analysis of greenhouse gas emissions associated with ethanol-to-jet (ETJ) SAF is conducted properly (https://ethanolproducer.com).

CHAPTER 4 – THE USE OF BIODIESEL AS DIESEL AUTO SUBSTITUTE

INTRODUCTION

The processing of organically derived oils with alcohol (methanol or ethanol), in the presence of a catalyst, to form methyl- or ethyl- esters produces the formation of biodiesel, which can be used either as neat fuel or blended with fossil diesel. In every geographical area the feedstock which is widely met or can be cultivated by human and produced in abundance, being favored by area's microclimate, is extensively used for biodiesel production. For example, Canada uses rapeseed, US soybean, Europe sunflower and Southern Asia palm. However, a wide variety of feedstocks, like mustard seed oil, palm oil, sunflower, rapeseed, soybean and jatropha, peanut and cotton seed are used for biodiesel production.

The production by edible vegetable oils is a serious concern the late years, because it has raised the food-versus-fuel debate that might has caused the high food prices, especially in the developing countries. It can also cause environmental issues due to the use of a wide area of arable land. Ecological imbalances and even climate changes are effected, as countries worldwide convert forests to farmland (deforestation). At this point the need of non-edible vegetable oil or second-generation feedstock for producing biofuels were introduced.

SHORT HISTORICAL DATA

The use of vegetable oil as fuel instead of conventional oil dates back in 1900. Especially, in the late eighteenth century, vegetable oil and animal fats were used for lighting purposes, whereas in 1893 German engineer Rudolph Diesel envisioned the potential of vegetable oil for powering agricultural oriented machines and thus he invented the combustion ignited diesel engine. French Otto Company demonstrated a peanut oil-fuel diesel engine in 1900 World's Fair in Paris and China, to produce a version of gasoline and kerosene, used tung oil and other vegetable oils. Moreover, in India, research on vegetable oil conversion to diesel during World War II has conducted (Chowhury, D.H., Mukerji S.N., Aggarwal, J.S and L.C. Verma, 1942, Indian vegetable fuel oils for diesel engines).

The first industrial-scale process for biodiesel production was developed in 1977 by Brazilian scientist Expedito Parente. In 1898, rapeseed was used for biodiesel production at the world's first industrial-scale plant, established in Asperhofen, Austria. In 1996, processing of waste grease into biodiesel was implemented commercially by the United States. In the late years (from 2000 onwards) biodiesel's popularity rose rapidly due to increased awareness of energy security, governmental tax subsidies and horribly high oil prices, especially after 2001.

Global concerns were raised initially during 2008, when the cost of crude oil exceeded the $100 per barrel, with continuous near-record high prices and depleting fossil fuel resources. National energy security of developed countries was forced by biodiesel production enforcement, which could reduce dependency on crude oil supply and exposure on extremely volatile oil prices. In late 1970s, Brazil initiated its biofuel program to counteract rising prices, which made Brazil today the world's largest producer and exporter of bioethanol (Singh R.S., Pandey A., Gnansounou E, CRC Press, 2017, Biofuels Production and Future Perspectives).

METHODS OF PRODUCTION

As mentioned before, in bioethanol section, biofuels are commonly classified as primary and secondary. Unprocessed biomass like fuel wood, wood chips and pellets are classified as primary biofuels (Roland Lee, Jean-Michel Lavoie, 2013, From First- to Third- Generation Biofuels:

Challenges of Producing a Commodity from a Biomass of Increasing Complexity, ResearchGate) and those produced by processing biomass into ethanol, biodiesel and dimethyl ether are classified as secondary biofuels (Francesco Cherubini, Sergio Ulgiati, 2010, Crop residues as raw materials for biorefinery systems – A LCA case study, Elsevier). Moreover, based on raw material, biofuels are divided into first-, second- and third- generation (Arthur Ragauskas et al., 2006, The Path Forward for Biofuels and Biomaterials, ResearchGate). Lately, discussions have come up for fourth- generation biofuels, as nicely presented in the following graph:

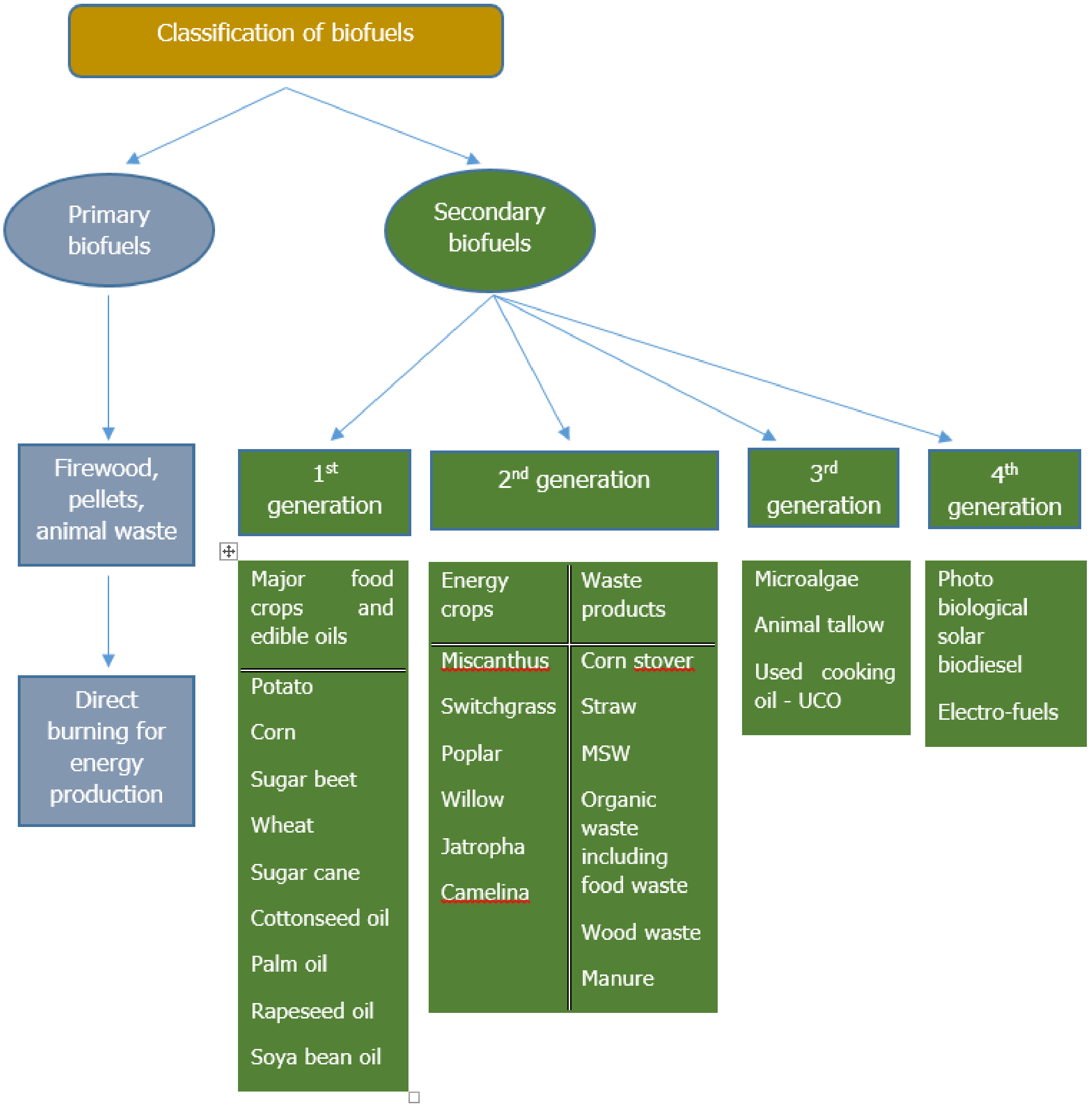


Figure 38. Classification of biofuels basis feedstock of production (Singh R.S., Pandey A., Gnansounou E, 2017, Biofuels Production and Future Perspectives, CRC Press)

First-Generation Liquid Biofuels

These are mainly produced from sugars and carbohydrate rich grains and seeds (Poonam Nigam, Anoop Singh, 2011, Production of liquid biofuels from renewable resources, ResearchGate). This category involves a relatively simple process of production of final product. Ethanol is the most popular first-generation biofuel, which as reviewed before, is produced by the fermentation of sugars. Sugarcane as discussed is the most widely used feedstock for bioethanol production, which is cultivated in Brazil and other tropical countries such as Australia, Peru, South Africa and India. Perennial grasses, sweet sorghum, maize and cassava are also quite basic feedstocks for bioethanol production. Sweet sorghum is widely grown in China, India, USA, Australia, Brazil, Zimbabwe and EU. Biodiesel is another first-generation fuel that is preferred from countries worldwide for sustainable energy management. Vegetable oils and oleaginous plants are the major sources through the transesterification processing, which involves alkaline, acidic or enzymatic catalysts and ethanol or methanol to convert lipids into fatty acids, with glycerin as the major by-product.

Lipids naturally include many compounds, such as fatty acids, glycerides, fat-soluble vitamins, cholesterols, phospholipids and glycolipids. The lipid-based biomasses, considered feedstocks for biofuels, consist of glycerides, because their primary structure consists of C8-C24 straight-chain fatty acids. The most common fatty acids generally found in lipid-bases biomasses are summarized in the table below:

Table 22 Commonly found fatty acids in glycerides for biofuels production

Common Name	**Number of Carbons**	**Number of Double Bonds**	**Shorthand Name**	**Molecular Weight**
Caprylic acid	8	0	C8:0	144.21
Capric acid	10	0	C10:0	172.26
Lauric acid	12	0	C12:0	200.32
Myristic acid	14	0	C14:0	228.37
Palmitic acid	16	0	C16:0	256.42
Stearic acid	18	0	C18:0	284.47
Oleic acid	18	1	C18:1	282.46
Linoleic acid	18	2	C18:2	280.45
Linolenic acid	18	3	C18:3	278.44

The distribution of fatty acids in glycerides, called fatty acid profile, is individually specified by the nature of each biomass type. For example, animal fat is typically composed of saturated fatty acids with high carbon numbers (up to 16 atoms) and thus it is solid in ambient temperature. In addition, the linear structure of saturated fatty acids allows the individual molecules to come closer to each other. On the contrary the molecules of "polyunsaturated fatty acids" ("PUFAs") are met in bent structures, as illustrated in the figure below:

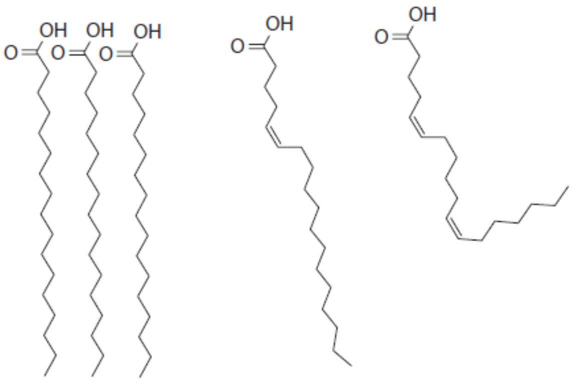


Figure 39 Chemical structure of saturated (three molecules of C18:0) and unsaturated fatty acids (C18:1 & C18:2)

Figure 39 Chemical structure of saturated (three molecules of C18:0) and unsaturated fatty acids (C18:1 & C18:2)

The glycerides, containing a large number of "PUFAs", are liquid at ambient temperature, because of the steric hindrance among chains. "PUFAs" are usually found in fish oils and on the other hand, oil plants, such as palm & coconut, have high numbers of saturated fatty acids, whereas others, such as olive and sunflower have a high amount of unsaturated fatty acids.

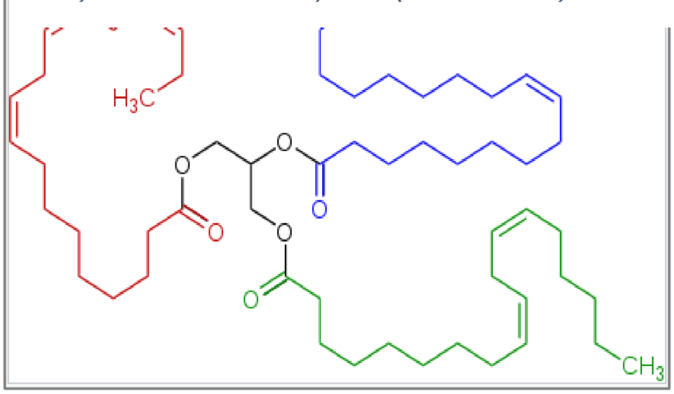


Figure 40 Glycerides chemical type

Figure 40 Glycerides chemical type

Glycerides include triglycerides, diglycerides and monoglycerides. Triglycerides are the main components of fats and oils and consist of three long-chain fatty acids linked to a glycerol backbone. As an example, the below triglyceride molecule, commonly found in linseed oil, is comprised from glycerol (center, black), linoleic acid (bottom right, green), a-linolenic acid (left, red) and oleic acid (top right, blue).

When the triglyceride reacts with an alcohol, the three fatty acids are released and combine with the alcohol to form alky- esters. This reaction, called transesterification, is a reverse process and can be accelerated with methanol over a catalyst in a liquid acid or liquid base. Methanol is normally used, although ethanol, 2-propyl, 1-butyl will also be appropriate.

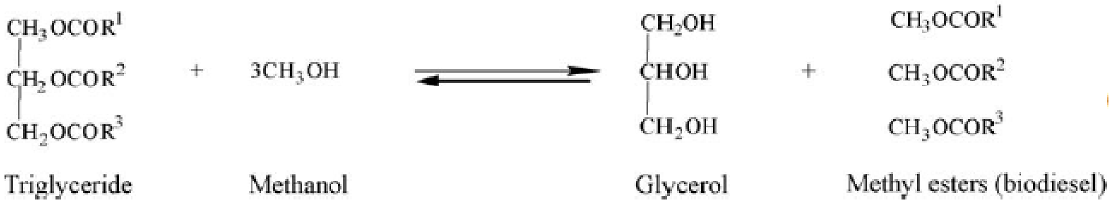


Figure 41 Transesterification of triglyceride over a liquid base catalyst

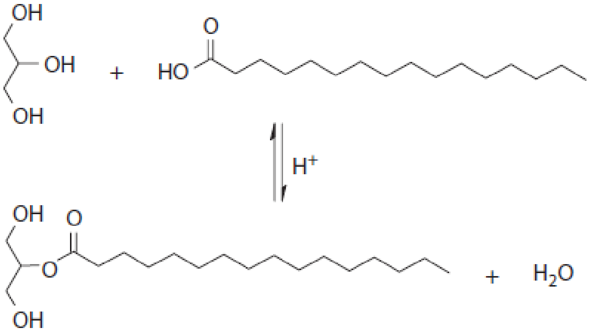


Figure 42 Acid-catalyzed esterification reaction between glycerol and palmitic acid (C16:0)

In the case that oil has a high content of Free Fatty Acids (FFAs) the above reaction is blocked, as the three hydroxyl groups of glycerol are completely esterified with three fatty acids to form triglyceride, as per pattern in figure 40.

Figure 42 Acid-catalyzed esterification reaction between glycerol and palmitic acid (C16:0)

Solid acid catalysts can simultaneously catalyze the transesterification of triglycerides and esterification of FFAs to methyl esters. Solid acid catalysts have the strong potential to replace the homogeneous catalysts, eliminating separation, corrosion and environmental problems.

The biodiesel feedstocks are considered to have lower yields than the bioethanol feedstocks. However, the yield is found to be higher for palm oil originated from tropical countries, such as those mentioned before. Palm oil accounts for about 10% of the total biodiesel production and it’s increasing rapidly due to farms in Indonesia and Malaysia (Greg Pahl, Bill Mckibben, 2008, Biodiesel: Growing a new energy economy, 2nd edition, Chelsea Green). Rapeseed oil is another one substantial biodiesel feedstock, coming from rapeseed – also known as canola – which is an annual herb grows in temperature regions ideally under 500 mm of annual rainfall. Rapeseed is mainly met to EU farm cultivations and account for about 59% of biodiesel production (Greg Pahl, Bill Mckibben, 2008, Biodiesel: Growing a new energy economy, 2nd edition, Chelsea Green). Soybean, also an important feedstock, is a legume crop with 17.5% oil content, albeit lower that palm oil. Soy accounts for 75%-90% of total biodiesel production (Singh R.S., Pandey A., Gnansounou E, 2017, Biofuels Production and Future Perspectives, CRC Press).

Second-Generation Liquid Biofuels

These are produced from either inedible food crop residues or inedible plant biomass such as grasses or trees explicitly grown for energy production. Their advantage compared to 1st generation biofuels is the elimination of dilemma "food availability for humans versus fuel production". Feedstocks of 2nd generation can be produced specifically for energy purposes with higher yields per unit-land. Moreover, it's believed that they have potential for lower overall energy cost and amount of waste production. For these reasons researchers usually enhance techniques like membrane filtration and integration of bio-refineries for improved yields.

Fundamentally two processes are followed, such as thermochemical and biochemical, to produce biodiesel from forests, agricultural and lignocellulosic biomass. Thermochemical processing defines the conversion of biomass by thermal decay and chemical reformation and essentially involves heating in the presence of different concentration of oxygen. In this processing group, direct **combustion**, **gasification**, **liquefaction** and **pyrolysis** are included.

Combustion

This is the chemical reaction between fuel and oxygen, which takes place in air. The products are carbon dioxide and water with the release of heat. Boilers burning biomass can be a sound substitute of combustion of conventional fossil fuel. Sulphur emissions are much lower and formation of particulate can be controlled at the source.

Gasification

Generally this is not a new technology by any means. Syngas can be produced from biomass by two routes; catalytic and non-catalytic. Non-catalytic requires a very high temperature (about 1.300 ^{o}C), whereas catalytic processing can be achieved in considerably lower temperature (lower than 900 ^oC). The gasification involves reaction of biomass with air, oxygen or steam to produce a mixture of CO, CO_2, H_2, N_2 and CH_4, known as synthesis gas or syngas. The production of syngas also leads to the production of methanol and hydrogen, two substance that are largely discussed to account for transportation in the forthcoming years.

Liquefaction

Liquefaction is converting biomass or organic material into stable liquid hydrocarbons under low temperature and high hydrogen pressure. The high-pressure liquefaction of air-dried wood provides bio-oils composed of a complex mixture of volatile organic acids and alcohols, aldehydes, ethers, esters, ketones, furans phenols, hydrocarbons and non-volatile components. Catalytic liquefaction is an efficient process to produce products with higher energy density in the liquid phase. The catalytic conversion is aided by using a catalyst or under high hydrogen partial pressure. How- ever, the technology poses many technical problems and has limited the utilization of the process.

Pyrolysis

Under this processing, heat is applied in the feedstock in anaerobic conditions (absence of oxygen) to break the long-chain molecules to their respective short-chain. Fast pyrolysis has demonstrated prominent results in producing concentrated fuel oils and recovering bio-fuels with medium-low calorific power. Biomass and waste are used as primary feedstock to produce syngas and other liquid fuels by varying the process conditions.

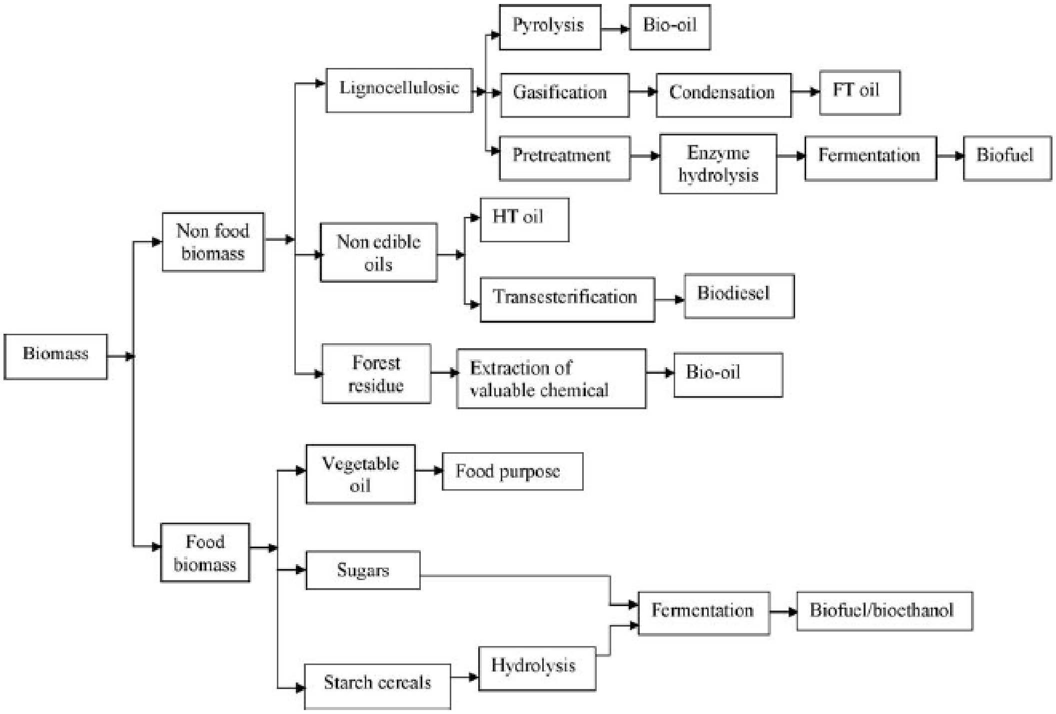


Figure 43 Tree schematic presentation of biomass alternative processing

Biochemical or biological processing includes the utilization of bacteria to convert biomass into gaseous products that are economically viable. These processes focus mostly on the polysaccharides, which is its main disadvantage compared to thermochemical techniques, which can practically convert all the organic compounds of biomass. Two main processes are used; anaerobic digestion and fermentation.

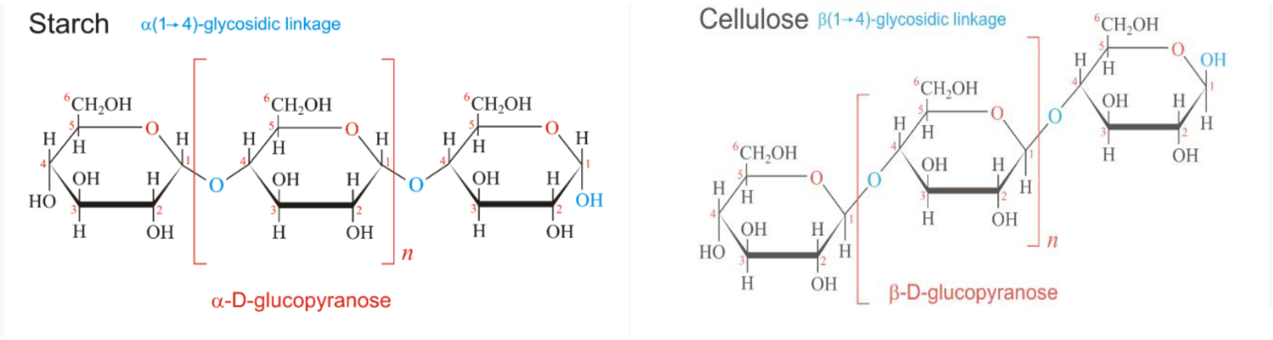


Figure 44 Starch and Cellulose chemical types, basic feed in biological processes

Figure 44 Starch and Cellulose chemical types, basic feed in biological processes

Anaerobic digestion

This method involves the digestion of microbial feedstock without oxygen to release heat carbon dioxide, methane and hydrogen sulphide. The process is carried out in large tanks, under ideal conditions, for several days. After digestion, the remaining solid digestate is used as fertilizers and the released gas (biogas) is burnt as fuel. The process is considered the most energy-effective and eco-friendly technology to produce biogas for heat and electricity generation, biosolids used for soil fertilizers and liquor used as liquid fertilizer.

Fermentation

The second technique has extensively been discussed in the ethanol production chapter of this thesis.

Third-Generation Liquid Biofuels

The third-generation biofuels are explicitly derived from microbes and microalgae via trans-esterification or hydrotreatment of the algal oil. These methods can efficiently increase the biofuel yield per year than the first generation biofuels that use traditional crops. The primary sources include resources that don’t affect the food chain and are feasible, readily available and flexible towards environmental parameters. These sources are majorly microalgae, animal oils, fish oil, waste cooking oil, animal fat etc. Another significant advantage involves the potential to decrease water pollution and unload waste handling facilities.

Microalgae are capable to produce 15-300 times more oil in comparison to traditional crops. Additionally, the conventional crop plants are harvested once or twice a year, whereas microalgae have a very short harvesting time of 10-30 days. This allows round year harvesting for multiple cycles per crop that will significantly increase the total algae biofuel yields. Integrated production of bioethanol and biodiesel is presented in following figure:

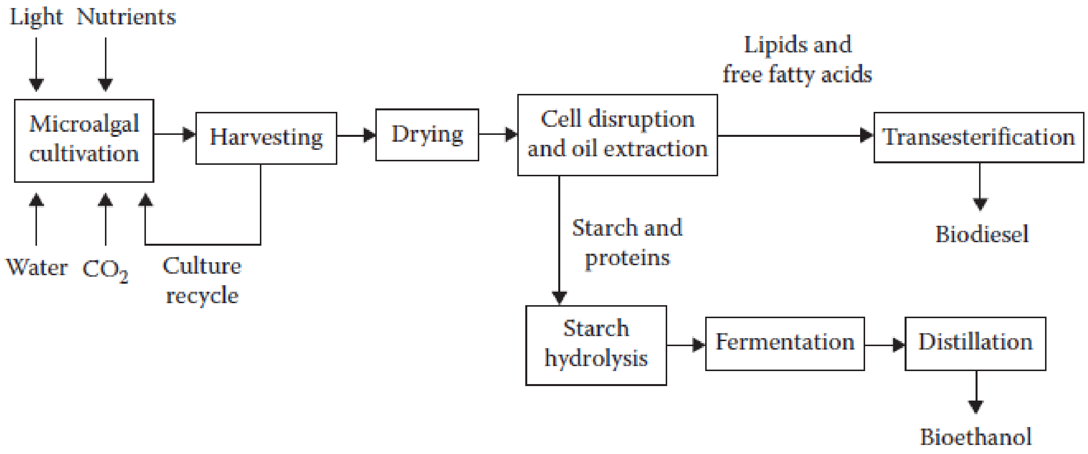


Figure 45 Biodiesel/Bioethanol Production processing from microalgae (Source: Niaik, S et al., Renew Enrgy, 35(8), 1624, 2010)

Fourth-Generation Liquid Biofuels

The fourth-generation biofuels are processed using genetically modified (GM) algae and photobiological solar fuels and electro-fuels. The genetically modified algae biomass is effective in producing biofuels, improving photosynthetic efficiency and increasing light penetration. The fourth-generation solar raw materials are widely available, economically cheaper and inexhaustible. The genetic modification of microalgal biomass holds a potential application in oil extraction methodology by inducing autolysis of cells and product secretary systems. Genome editing tools such as zinc-finger nuclease (ZFN), transcription-like effector nucleases (TALEN), and clustered regularly interspaced palindromic sequences (CRISPR/Cas9) are widely used bioinformatics tools.

Biodiesel production methods tested repeatedly and used widely on industrial scale are the following:

- In 1st gen. fuels the long-chain hydrocarbons (C30 and more) extracted from herbaceous plants, are cracked to biodiesel. The same cracking method can be used on the treatment of hydrocarbons accumulated by some microalgae.
- In 2nd gen. biofuels, biomass or waste through pyrolysis can form bio-oil, which can be converted to biodiesel.

- Gasification of biomass followed by Fischer-Tropsch synthesis is another common production technique of 2nd gen. biofuels.
- The transesterification of plant, animal, waste oils and fats to methyl esters, i.e. biodiesel is another way for 1st gen. fuels to be produced.
- Oil accumulated by some microalgae, extracted and transesterified into biodiesel is a 3rd gen. production application.

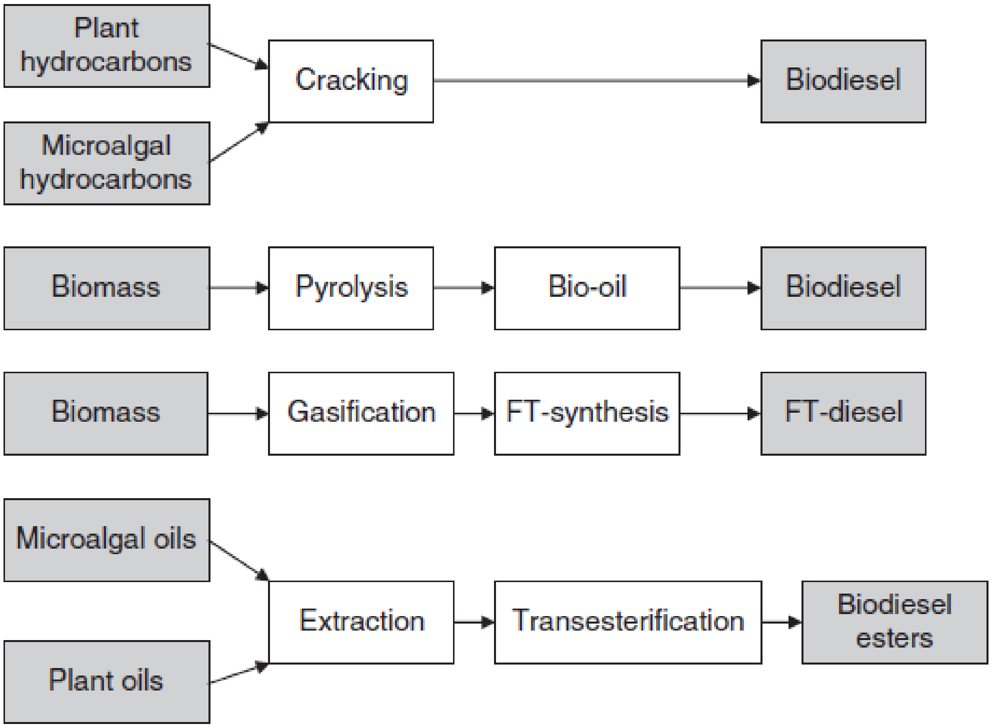


Figure 46 Different routes for alternative diesel production

Synthetic Diesel, Fischer-Tropsch Synthesis

This method was developed back in the 1930s, and comprises several chemical reactions that convert a mixture of carbon monoxide (CO) and hydrogen (H2) into long chained hydrocarbons with similar properties to crude oil products.

A gas containing as its main components H_2 and CO can be produced by the high-temperature gasification of coal, biomass and waste, and is known as syngas. The gasification process produces a mixture of CO, H_2, methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2) and water (H_2O). Natural gas can also be used in the FT process. The FT synthesis was used to produce diesel and petrol in World War II using coal as the starting material. Syngas is mainly used by the chemical industry (Fig. 45) for ammonia production and by the refinery industry to produce hydrocarbon-based fuels, so called "gas to liquid" (GTL) fuels. To make the process sustainable, coal and gas should be replaced with biomass and waste materials.

In general, there are two industrial methods of producing syngas from biomass: a fluidized bed gasifier and entrained flow gasifier. The fluidized bed gasifier converts biomass using an air-blown circulating fluidized bed operating at 900°C, but as the gas formed is not clean the system requires a catalytic reformer to remove many of the contaminants (Fig. 45). The gas from the fluidized bed gasifier contains H_2, CO, CO_2, H_2O and considerable amounts of hydrocarbons such as CH_4, benzene and tars. The second option is entrained flow gasification where higher temperatures (1300°C) are used. This system requires a supply of very small particles to burn correctly so that any material used has to be milled, which is energy-intensive and makes handling difficult.

No matter which method is used to produce the gas, extensive syngas cleaning and conditioning are required before the FT process can be used to produce liquid fuels as the contaminates inhibit the catalyst. The syngas also needs to have a H_2/CO ratio of 2:1. The concentration of CO and H_2 can be adjusted in the water shift reactor which converts CO to H_2 and CO_2.

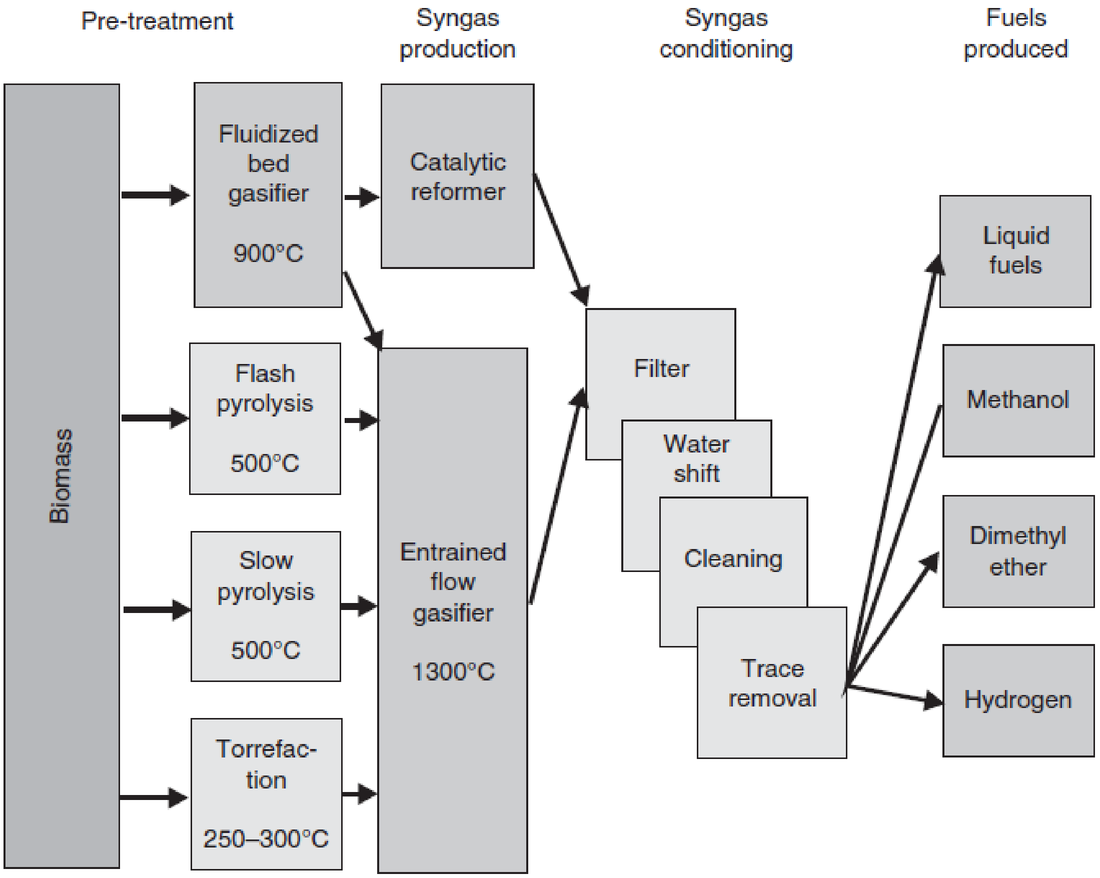


Figure47 Syngas preparing for FT synthesis (van der Drift and Boerrigter, 2006).

WHERE BIODIESEL IS PRODUCED

In 2023, international markets are widely trading two different types of renewable diesel:

1. Biodiesel, which refers to traditional biodiesel, FAME (Fatty Acid methyl Ester) produced by the transesterification of animal fats, fish fats, used cooking oil, vegetable oils, with methanol.
2. HVO, which refers to the Hydrogenated Vegetable Oil, which is a mixture of paraffinic hydrocarbons obtained by hydrocracking or hydrogenation of vegetable oils.

The EU is the largest producer of biodiesel worldwide, followed by the US. Renewable diesel (HVO and biodiesel) total production in EU amounted to about 15.7 – 16.6 million cubic meters in 2019, equal to around 14 million tons (considering biodiesel density of 0.88 g/cm3). The production volumes raised slowly in the last 5 years, also thanks to the contribution of hydrogenated vegetable oil.

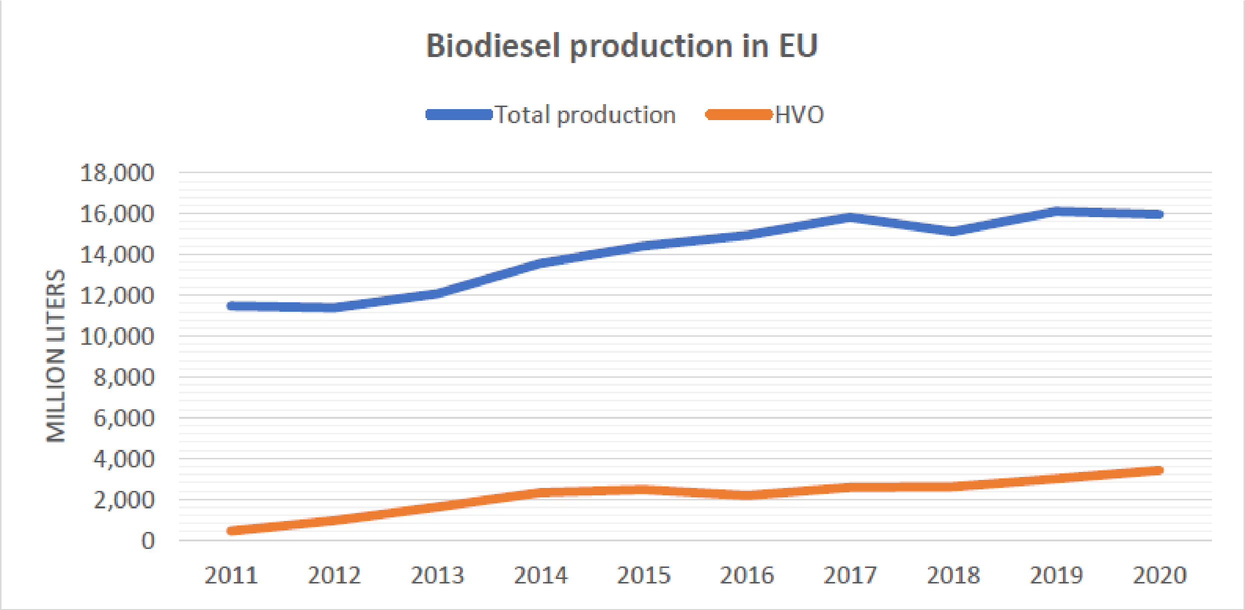


Figure 48 Biodiesel and HVO production volume in EU transportation sector, BIKE data (www.bike-biofuels.eu/the-project)

As reported in the figure below, the biofuels consumption in EU raised constantly until 2012, when Low ILUC directive was introduced amending the targets of the renewable energy directive. After the decrease occurred from 2012 and 2013, the global production re-started to slightly increase. However, the increase was only partially driven by the take-off of advanced biofuels production. In fact, conventional 1st generation biofuels still represented the largest market portion, and strongly contributed to the growth of biofuels blending until 2019. In 2019, COVID-19, consumption of bioethanol amounted to about 1.4% and renewable diesel (including HVO) reached the 6.4 % of consumed transport fuels in Europe, for a total biofuels consumption of around 7.8%. The rise of bioethanol consumption was slight and almost equal to the level of 2011. In contrast, consumption of biodiesel and HVO has increased.

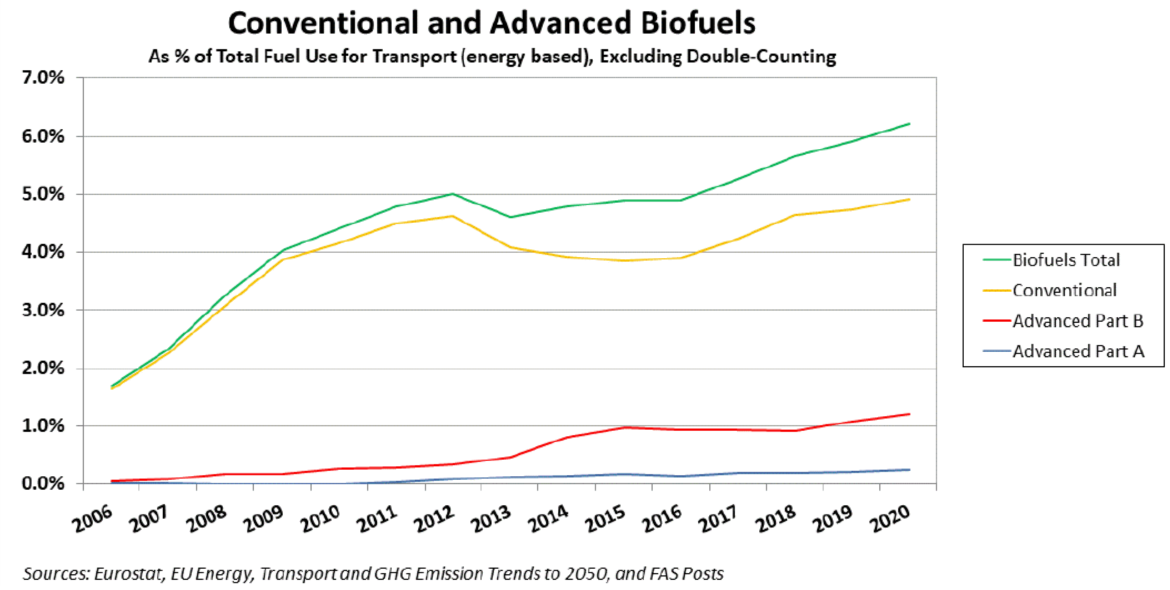


Figure 49 Conventional vs Advanced Biofuels, Eurostat data (EurObserv'ER / Eurostat database)

WHERE BIODIESEL IS BEING CONSUMED AND WHAT'S THE FUTURE PERSPECTIVES

In Europe most of EU members' diesel market in tuned to E7 (7% v/v of biodiesel blended to 93% of fossil diesel). However, some member states have allowed biodiesel to be above 7%. Whilst, for example, France has approved B10 several years ago, Belgium and Spain have recently introduced higher than 7% diesel grade in their markets.

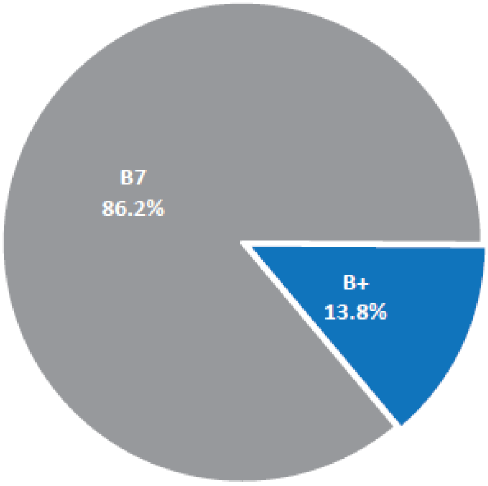


Figure 50 B7 adaption by EU countries, Eurostat data [36]

In 2021, the biodiesel incorporation rate across the EU-27 was 7.3 in energy terms and 7.9% in volumes. Biodiesel consumption, including renewable diesel – HVO, increased by 3.3% vs. 2020, to reach a historic high of 13,605 ktoe.

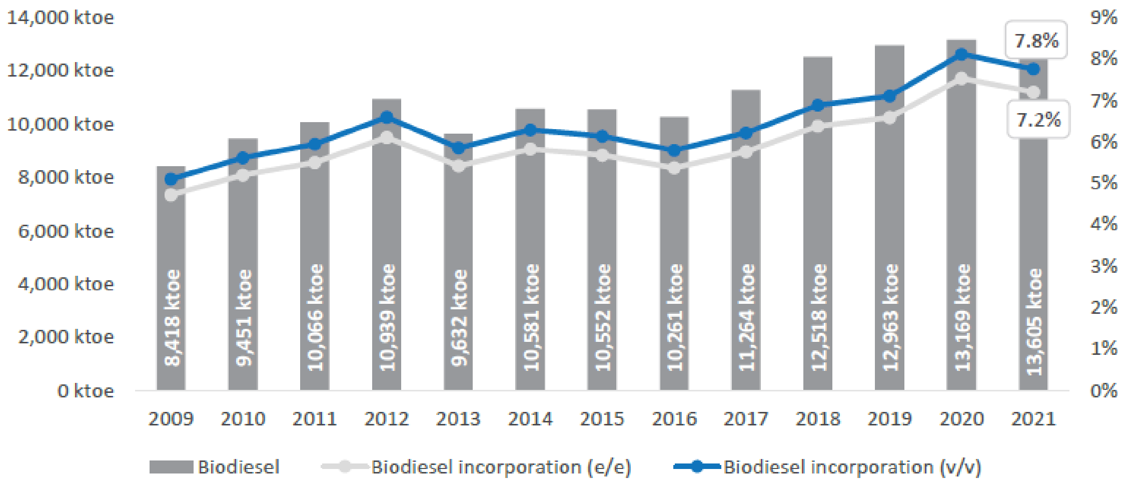


Figure 51 Biodiesel usage integration by EU members, Eurostat data (EurObserv'ER / Eurostat database)

In US according to Energy Information Administration (EIA), the years between 2014 and 2018 the consumption of biodiesel (excluding HVO) in the States were significantly above domestic production reaching the highest of 5 mil barrels per year (2017). In 2019 onwards the pullback of consumption at lower than 4 mil barrels per annum levels, has effected the production to meet sharply the demand for biodiesel.

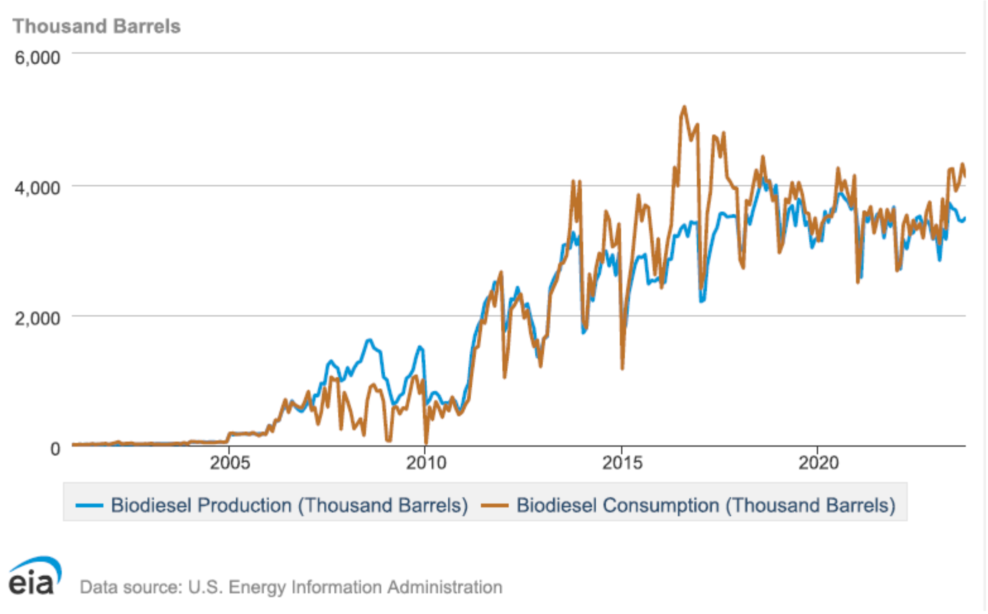
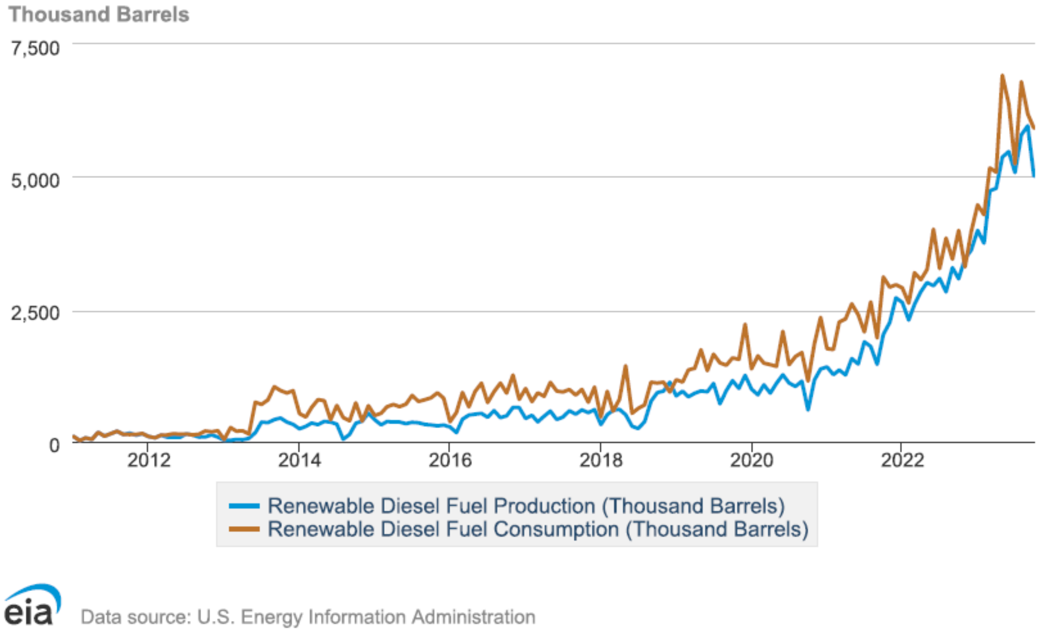


Figure 51 Biodiesel penetration in US, EIA data

In respect of HVO, or alternatively common known as Renewable Diesel Fuel, data illustrates intensely that after 2020 the increase in production and consumption have compensated largely the lower barrels of biodiesel used as blending components in US transportation fuel market. In the fig. 51, we can clearly notice how steep the increase of figures in supply and demand is after the year of 2022, climbing up to nearly 7 mil barrels per annum.



Data source: U.S. Energy Information Administration

Figure 52 HVO penetration in US, EIA data

CHAPTER 5 - CURRENT AND FUTURE LEGISLATION TO BACK UP BIOFUELS

INTRODUCTION

The developments on the field of biofuels and the speed and the extent that these developments will come in place, has largely to do with the legislation regarding mainly the CO_2 but also the rest of Green House Gases (GHG) emission reductions targets. Those targets are imposed to the Nations by Governmental Authorities in the effort to incorporate the directives of European Union and US Government's policies. Apart from EU and US several other countries with higher or lower sensitivity to environmental pollution evolvements are releasing their own environment protection and clean air/waters preservation policies and regulations.

LEGISLATION IN EUROPE

In principal the regulatory bodies in the European Union (EU) are the:

- Parliament, explicitly elected by the people of Member States
- Council, which represents the government of the Member States
- Commission, the executive and the body having the right to initiate legislation

Legislation across Union's members can be classified as following:

- ➢ Regulations, are the most direct form of law. They have binding legal force in all Member States, on a par with national laws. National governments don't need to take action to implement EU regulations. They are passed either jointly by the EU Council and Parliament or by the Commission alone.
- ➢ Directives are addressed to national authorities that should make actions to make them part of their national law. Directives may concern one or more Members or all of them.
- ➢ Decisions apply only in specific cases and involve particular authorities or individuals. They can come from the EU Council (sometimes jointly with the European Parliament) or the Commission. They can require authorities and individuals in Member States either do something or stop doing something, and can also confer rights on them.

The EU’s standard decision-making procedure is known as “codecision”. This means that the directly elected European Parliament has to approve EU legislation together with the Council (the governments of the 28 EU countries).

The first renewable energy directive 2009/98/EC had set a target for renewable energy consumption at 20% by 2030 and specifically the target for biofuels usage in transportation was defined to reach the 10% of total primary energy consumption in the EU transportation sector. In 2010 the total biofuel consumption represented about 4,7% of all transportation fuel consumption, but the amount was given mainly by first generation biofuels, typically produced from feedstock cultivated on cropland that was previously used for other agricultural crops, such as growing food or feed. This is known as **Indirect Land Use Change** (ILUC) and it has a direct impact on the carbon footprint of value chains, negating the greenhouse gas savings that result from increased biofuels consumption. For that reason, in 2012 the ILUC Directive was integrated to the RED 2009/98/EC. According to ILUC Directive, for fulfilling the target of 10% renewable energy usage, only 7% biofuels from food crops could be counted. In 2016 the European Commission published the first version of the package “Clean Energy for all Europeans” in which a much better address of ILUC Directive was attempted. As part of this package, EU institutions approved a revised version of Renewable Energy Directive 2009/98EC, named for simplicity as RED II, which entered into force in December 2018 (Directive EU/2018/2001). In the new RED II the overall EU target for renewable energy consumption was raised to 32% by 2030. RED II sets a target for biofuels consumption in transport sector to 14% within 2030, but with strong limits to the consumption of high ILUC-risk biofuels, bio-liquids and biomass fuels with a significant expansion in land with high carbon stock. These limits consist of a freeze first generation biofuels consumption at 2019 levels for the period 2021-2023, which will gradually decrease from the end of 2023.

From 31 December 2023 until 31 December 2030 at the latest, that limit of first generation biofuels share shall gradually decrease to 0%. At the same time, the RED II specifies the biomass feedstock suitable for the production of advanced, low-ILUC risk biofuels. Within the 14% transport sub-target, there is a dedicated target for advanced biofuels produced from feedstocks listed in Part A of Annex IX (https://www.transportpolicy.net/ & https://www.sustainablefuels.eu/policy-priorities/fuel-quality-directive/).

Table 23 RED II – Part A and Part B of ANNEX IX

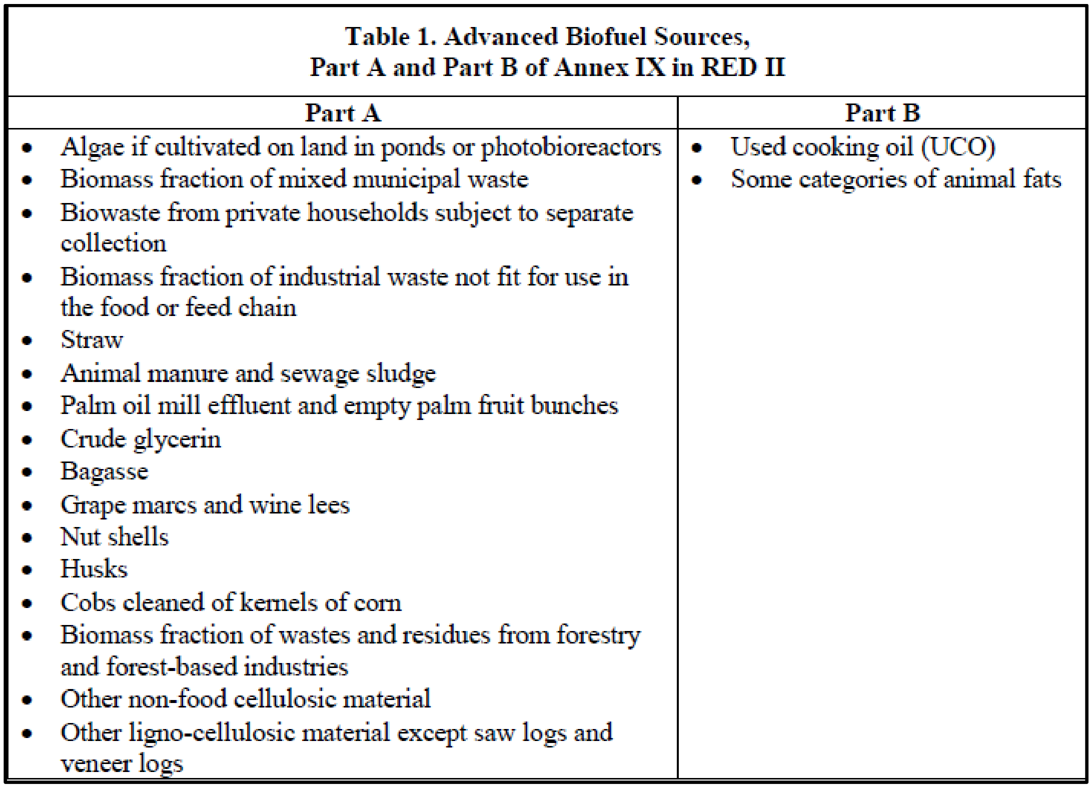


Table 1. Advanced Biofuel Sources,
Part A and Part B of Annex IX in RED II

Part A	Part B
• Algae if cultivated on land in ponds or photobioreactors • Biomass fraction of mixed municipal waste • Biowaste from private households subject to separate collection • Biomass fraction of industrial waste not fit for use in the food or feed chain • Straw • Animal manure and sewage sludge • Palm oil mill effluent and empty palm fruit bunches • Crude glycerin • Bagasse • Grape marcs and wine lees • Nut shells • Husks • Cobs cleaned of kernels of corn • Biomass fraction of wastes and residues from forestry and forest-based industries • Other non-food cellulosic material • Other ligno-cellulosic material except saw logs and veneer logs	• Used cooking oil (UCO) • Some categories of animal fats

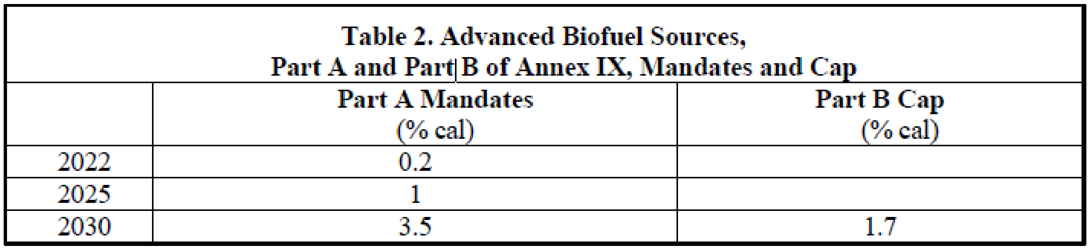


Table 2. Advanced Biofuel Sources,
Part A and Part B of Annex IX, Mandates and Cap

	Part A Mandates (% cal)	Part B Cap (% cal)
2022	0.2	
2025	1	
2030	3.5	1.7

The contribution of advanced biofuels and biogas produced from the feedstock listed in Part A of Annex IX as a share of final consumption of energy in the transport sector shall be at least 0,2% in 2022, at least 1% in 2025 and at least 3,5% in 2030. Biofuels produced from feedstock listed in Part B (those obtained from UCO and animal fats) will be capped at 1.7 percent in 2030. In the revised REDIII, advanced biofuels listed in Annex IX and renewable fuels of non-biological origin will be double counted towards both the 3.5 percent target and towards the 14 percent target.

Summarizing the above supported from EU biofuels will be those defined as “advanced” and “Low ILUC risk”. The latter biofuels are defined as those produced from feedstocks that avoid displacement of food and feed crops, through improved agricultural practices or through cultivation of areas not previously used for crop production.

In July 2021, the European Commission adopted the “Fit for 55” package to help the Union reach the target of 55% GHG emissions savings reduction by 2030 compared to 1990 levels. Under that package the Commission suggested some amendments to RED II which raise its ambitions, but widely maintain the framework for biofuels.

But how much were the GHG emissions in EU in 1990? Below chart, as retrieved from Eurostat, shows that they were 4,9 billion metric tons of carbon dioxide equivalent (MtCO₂e). In 2021, GHG emissions were 3,5 MtCO₂e an increase of five percent from the COVID-19 induced slump in 2020. Nevertheless, EU GHG emissions remained below pre-pandemic levels in 2021.

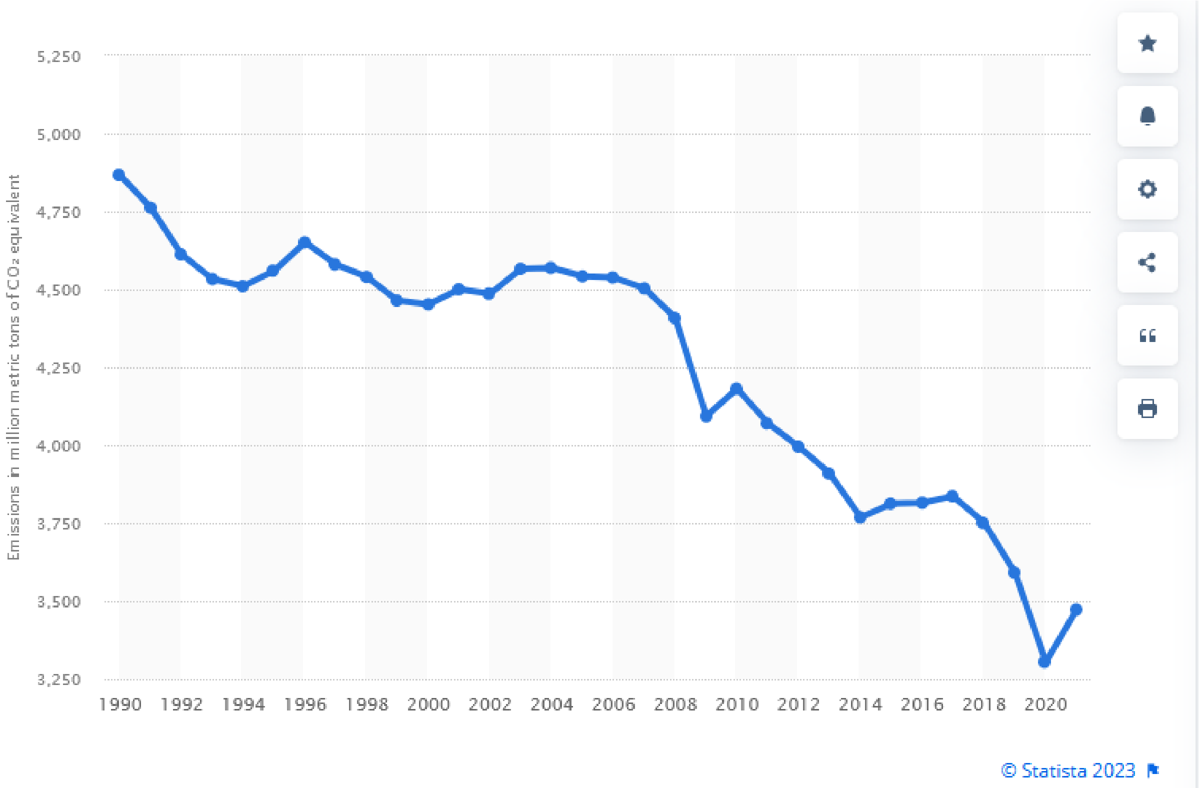


Figure 53 Emissions in mil MT of Co2 equivalent, Statista data

In the transportation sector, due to the growth in passenger transport and inland freight volumes, figures directly related to economic growth potential, the EU’s transport emissions increased between 2013 and 2019. The emissions then decreased by 13.6% between 2019 and 2020, because of a drastic decrease in transport activity during the COVID-19 pandemic. According to preliminary estimates, emissions increased by 7.7% in 2021, following a rebound effect of the economy. For comparison, in the years following the economic crisis a decade ago, emissions decreased by 1-3% per year.

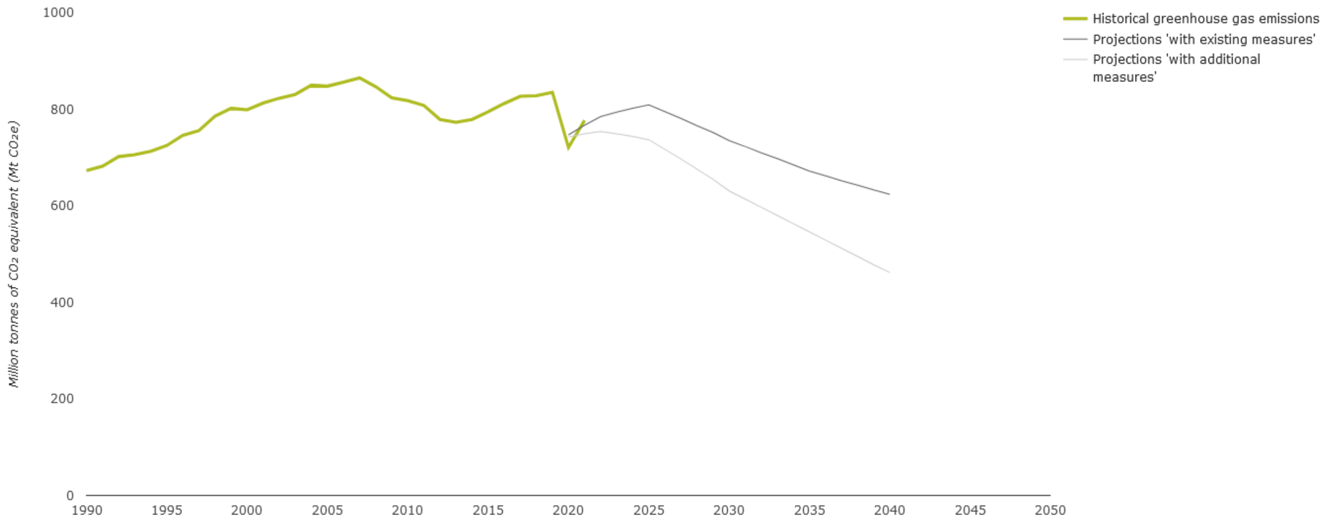


Figure 54 Emissions drop from 2020 onwards

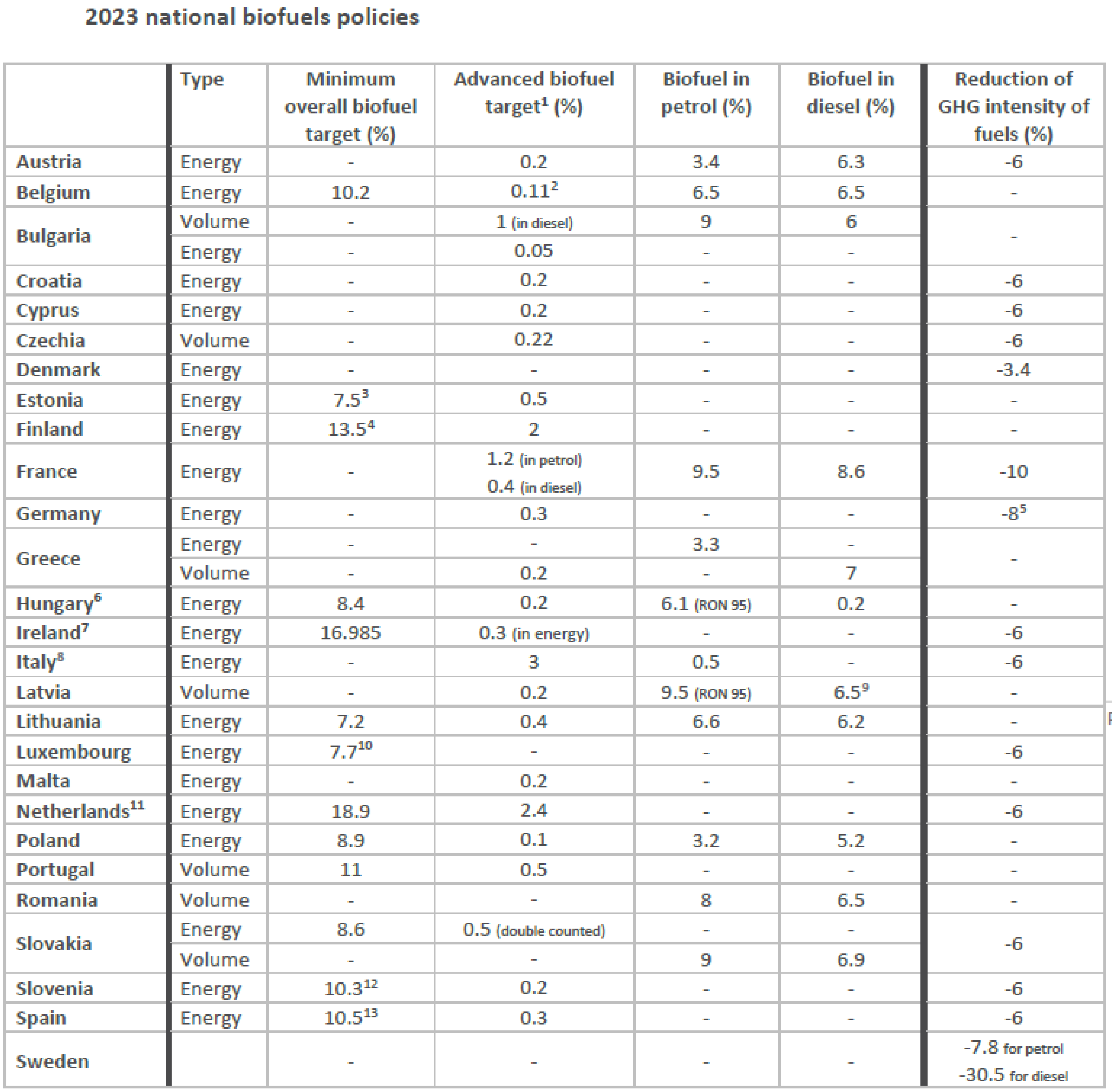
National projections indicate that Member States expect an increase in transport emissions in the coming years. Without the implementation of additional measures, an increase could be observed until 2025, while the subsequent projected reductions would still leave transport emissions in 2030 around 9% above 1990 levels. If Member States implement the additional measures planned to reduce transport emissions, these would peak in 2022 and be reduced thereafter. With these additional measures, 2030 emissions would reach a level of 6% below 1990 levels. Most planned policies and measures in the transport sector focus on promoting low-carbon fuels or electric cars, as well as encouraging a modal shift to public transport.

In addition to domestic transport, international aviation and international maritime sectors contribute to overall emissions related to transportation. GHG emissions from these sectors have increased since 1990. Among the domestic transport categories, only emissions from domestic navigation and railways have decreased since 1990. Furthermore, only road transport emissions are projected to decrease until 2030.

Road transport constitutes the highest proportion of overall transport emissions — in 2020 it emitted 77% of all EU transport GHGs (including domestic transport and international bunkers). As a majority of existing and planned measures in the Member States focus on road transport, this share is expected to decrease as road transport decarbonises faster than other transport modes. The largest increases up to 2030 are projected in the aviation sector, followed by international maritime transport, as they are not prioritised by national policies. These sub-sectors are therefore expected to constitute a higher proportion of transport sector emissions in the coming years.

Aviation was particularly affected by the COVID-19 pandemic, with international aviation emissions 58% lower in 2020 than in 2019. However, a drop in emissions due to the pandemic was temporary. Air traffic activity rose by 22% in 2021 and flight numbers are expected to return to 2019 levels by 2023 at the earliest (https://www.eea.europa.eu/en/analysis/indicators/greenhouse-gas-emissions-from-transport#footnote-FXG68KAW).

Table 24 2023 EU members' national biofuels policies (Biofuel Mandates in the EU by Member State (report) – 2023 Foreign Agricultural Service)



2023 national biofuels policies

	Type	Minimum overall biofuel target (%)	Advanced biofuel target[1] (%)	Biofuel in petrol (%)	Biofuel in diesel (%)	Reduction of GHG intensity of fuels (%)
Austria	Energy	-	0.2	3.4	6.3	-6
Belgium	Energy	10.2	0.11[2]	6.5	6.5	-
Bulgaria	Volume	-	1 (in diesel)	9	6	-
	Energy	-	0.05	-	-	
Croatia	Energy	-	0.2	-	-	-6
Cyprus	Energy	-	0.2	-	-	-6
Czechia	Volume	-	0.22	-	-	-6
Denmark	Energy	-	-	-	-	-3.4
Estonia	Energy	7.5[3]	0.5	-	-	-
Finland	Energy	13.5[4]	2	-	-	-
France	Energy	-	1.2 (in petrol) 0.4 (in diesel)	9.5	8.6	-10
Germany	Energy	-	0.3	-	-	-8[5]
Greece	Energy	-	-	3.3	-	-
	Volume	-	0.2	-	7	
Hungary[6]	Energy	8.4	0.2	6.1 (RON 95)	0.2	-
Ireland[7]	Energy	16.985	0.3 (in energy)	-	-	-6
Italy[8]	Energy	-	3	0.5	-	-6
Latvia	Volume	-	0.2	9.5 (RON 95)	6.5[9]	-
Lithuania	Energy	7.2	0.4	6.6	6.2	-
Luxembourg	Energy	7.7[10]	-	-	-	-6
Malta	Energy	-	0.2	-	-	-
Netherlands[11]	Energy	18.9	2.4	-	-	-6
Poland	Energy	8.9	0.1	3.2	5.2	-
Portugal	Volume	11	0.5	-	-	-
Romania	Volume	-	-	8	6.5	-
Slovakia	Energy	8.6	0.5 (double counted)	-	-	-6
	Volume	-	-	9	6.9	
Slovenia	Energy	10.3[12]	0.2	-	-	-6
Spain	Energy	10.5[13]	0.3	-	-	-6
Sweden		-	-	-	-	-7.8 for petrol -30.5 for diesel

Mandate Changes in Response to Crisis

Russia’s invasion in Ukraine in February 2022 resulted in a steep increase in energy and agricultural commodity prices, which in turn increased inflation. As a response and to alleviate inflationary pressure for their consumers and compliance pressure on industry some countries decided to temporarily reduce biofuel mandates or the penalties for not fulfilling the mandates for their territory (Biofuel Mandates in the EU by Member State (report) – 2023 Foreign Agricultural Service & Overview of biofuels policies and markets across EU (ePURE – European renewable ethanol)):

- Croatia removed some of the penalties for not achieving the blending thresholds for fuel distributors. This measure was valid from March through December 31, 2022. From January through June 2023, the penalties were reinstated but at a very low level.
- Czech Republic made blending mandates voluntary as of July 1, 2022. This measure was part of a legislative package adopted by the Czech government in May 2022. However, the obligation for suppliers to reduce the GHG emissions remains in place.
- Finland temporarily reduced its 2022 and 2023 mandates to alleviate high fuel prices for consumers.
- Latvia suspended mandatory blending of biofuels for the period of July 1, 2022, through December 31, 2023. During this period, biofuel blending in gasoline and diesel is voluntary.
- Poland set the minimum level of fulfilment of the National Indicative Target (NIT) in 2023, which entitles the operators to use the substitution fee mechanism, at 80 percent (maintaining the reduced level as in 2020-2022). The new legislation also extended the possibility of using the 0.82 reduction factor for another year, lowering the mandatory blending for diesel fuel to 5.2 percent (the limit set at 6.2 percent level, but reduced in 2020 to 5.0 percent), and raising to 0.9 percent the limit on the possibility of using HDRD in meeting the NIT. The amendment also raised the limit on the use of bio-components produced from certain raw materials such as algae, bio-waste, biodegradable municipal waste, straw, biomass fractions from forest management, among others to 0.5 percent (from 0.45 percent in 2020-22).
- Sweden froze annual increases to the GHG emissions reduction targets in 2023.

Future EU Legislation – Latest Amended REDIII Including RefuelEU Aviation & RefuelEU Maritime Regulatory Schemes

The latest revision of EU/2018/2001 came into force on November, 20th 2023 under the need the EU to speed up the clean energy transition. There will be an 18-month period to incorporate directive's provisions into national law, with a shorter deadline of July 2024 for some provisions related to renewables permits (European Commission official site).

The overall renewable energy sources target (RES-T) in 2030, i.e. the share of energy from renewable sources in the Union's gross final consumption of energy, has been updated to 42,5% the minimum. On voluntary basis can even be increased up to 45%.

In regard to the transportation segment each Member state shall set an obligation on fuel suppliers to ensure that the amount of renewable fuels and renewable electricity supplied to the transportation sector leads to a share of renewable energy within the final consumption of energy in the transportation sector of at least 29% by 2030 or to a greenhouse gas density reduction of at least 14,5% by 2030. Members shall report on the share of renewable energy within transportation sector, including the maritime section, as well as on the greenhouse gas intensity reduction. Recycled carbon fuels might be taken into account for the calculation of the target if their GHG savings are at least 70%. For the calculation of RES-T also the energy supplied to maritime transport shall be included but limited to 13% (Cyprus and Malta have secured a waiver for a limit of 5%).

In terms of biodiesel usage, the combined share of advanced biofuels and biogas produced from the feedstock quoted in Part A of Annex IX and of renewable fuels of non-biological origin shall be at least 1% in 2025 and 5,5% in 2030, of which a share of 1% min should be RFNBOs in 2030. Also, those listed in Part B of Annex IX needs to be boosted and their share shall be at least 1,7% by 2030.

But the European Commission has conducted provisions not only for transportation but also for aviation and maritime sector. More precisely, under **ReFuelEU Aviation** regulation, Commission sets RES-T as per below plot that need to be adopted for commercial air transport flights, in all Union airports with:

- passenger traffic higher than 800.00 passengers or
- freight traffic higher than 100.000 ton compared to previously reported period (time base of 1 year)
- and they are not in the outmost regions

where SAF stands for Sustainable Aviation Fuel and its definition is:

Synthetic Aviation fuels - renewable fuels of non-biological origin (RFNBOs), produced from renewable or nuclear energy or *Aviation biofuels* – advanced biofuels – advanced biofuels or biofuels produced from Annex IXB feedstock or other biofuels which comply with the sustainability and lifetime emission savings criteria according to REDII with the exception of biofuels produced from "food and feed crops" or *Recycled carbon aviation fuels*.

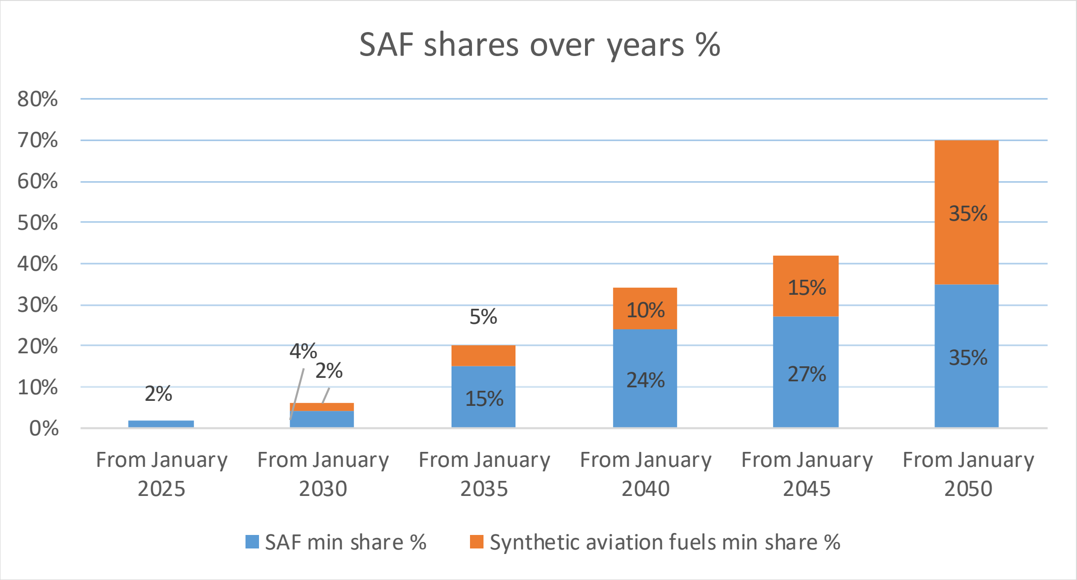


Figure 55 SAF shares on aviation sector

Under **ReFuelEU Maritime** scheme, ships are obliged to reduce their annual average GHG intensity of energy used onboard, starting from 2025. In particular the timeline that has been set corresponds to the adjacent plot. The GHGs that count are CO_2, CH_4, and N_2O and the methodology to be used for calculations is the Life cycle (Well-to-Wake) evaluation of marine fuels. The reference value to be used for emission reduction calculations shall be the 91,16 grams of CO_2 equivalent per MJ.

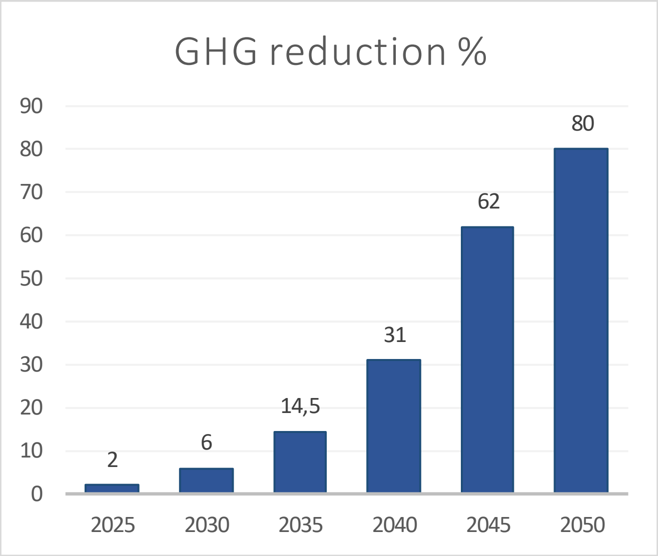


Figure 56 ReFuelEU Maritime provisions

Figure 56 ReFuelEU Maritime provisions

LEGISLATION IN USA

In 2020 the U.S. Environmental Protection Agency celebrated the 50-year anniversary of the signing of the Clean Air Act Amendments, a landmark piece of legislation that has led to significant environmental and public health benefits across U.S. The Clean Air Act is the law that defines the regulations imposed to States by a National Agency, called Environmental Protection Agency (EPA) that was founded to protect and improve the Nation’s air quality and the stratospheric ozone layer. The last major change in the law, was the aforesaid Clean Air Act Amendments, which was enacted by Congress in 1990.

Now, let’s illustrate how a law is being created in USA within 3 steps, as per below:

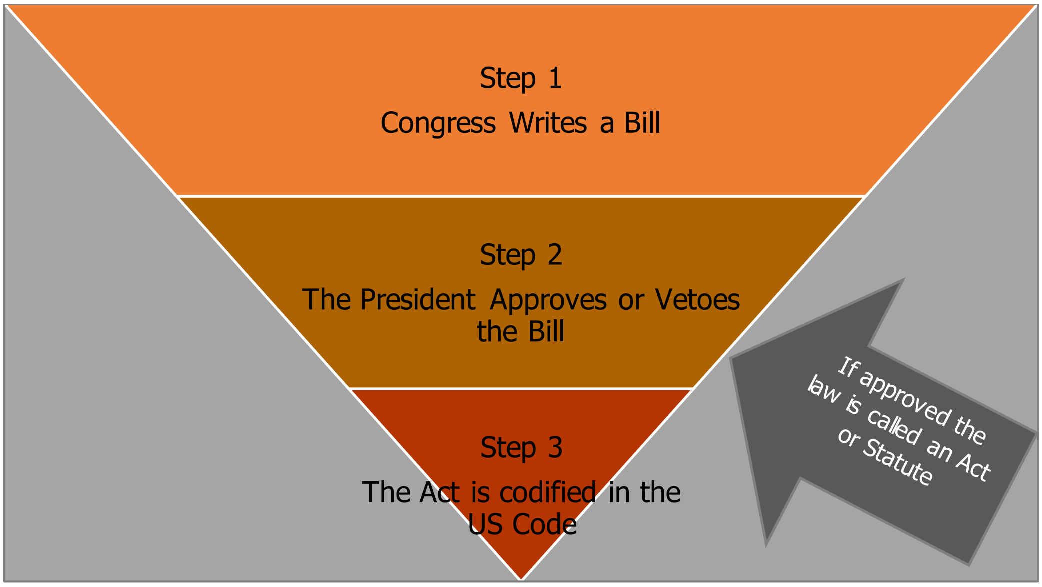


Figure 57 US legislation pathway

Laws often do not include all the details needed to explain how an individual, business, state or local government, or others might follow the law. In order to make the laws work on a day-to-day level, Congress authorizes certain government agencies - including EPA - to create regulations. Also creating a regulation also has 3 steps, as per below:

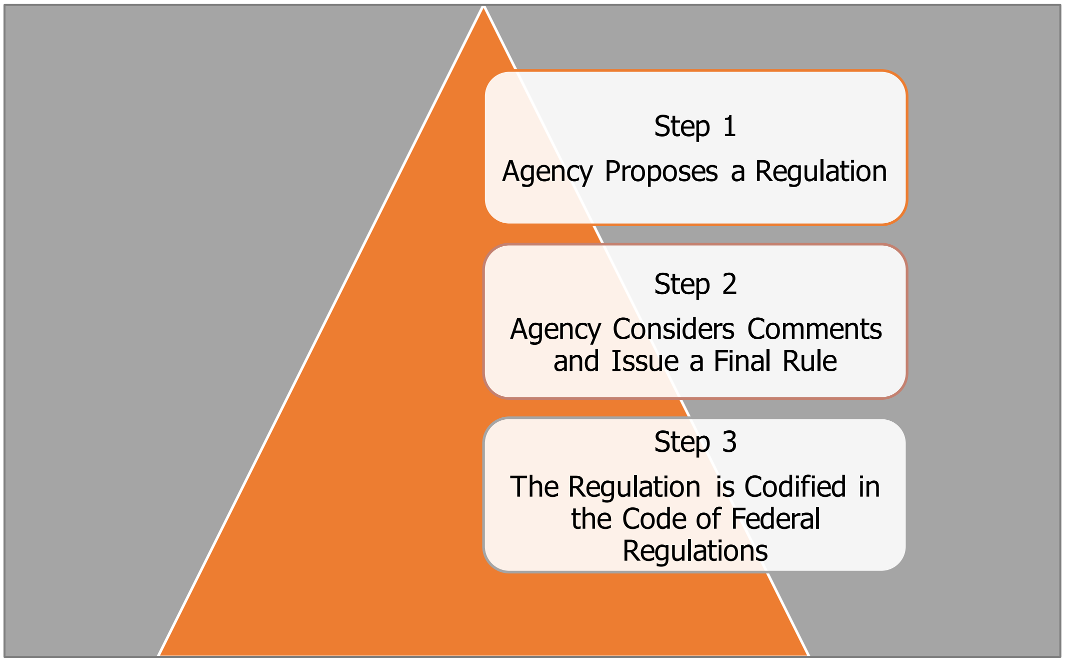


Figure 58 US regulations step process

The Clean Air Act has predicted actions in many different fields as anyone can see in the following table of contents. Title II describing the regulations for lowering emissions from moving sources, including motor vehicles (part A) applies to the oil business.

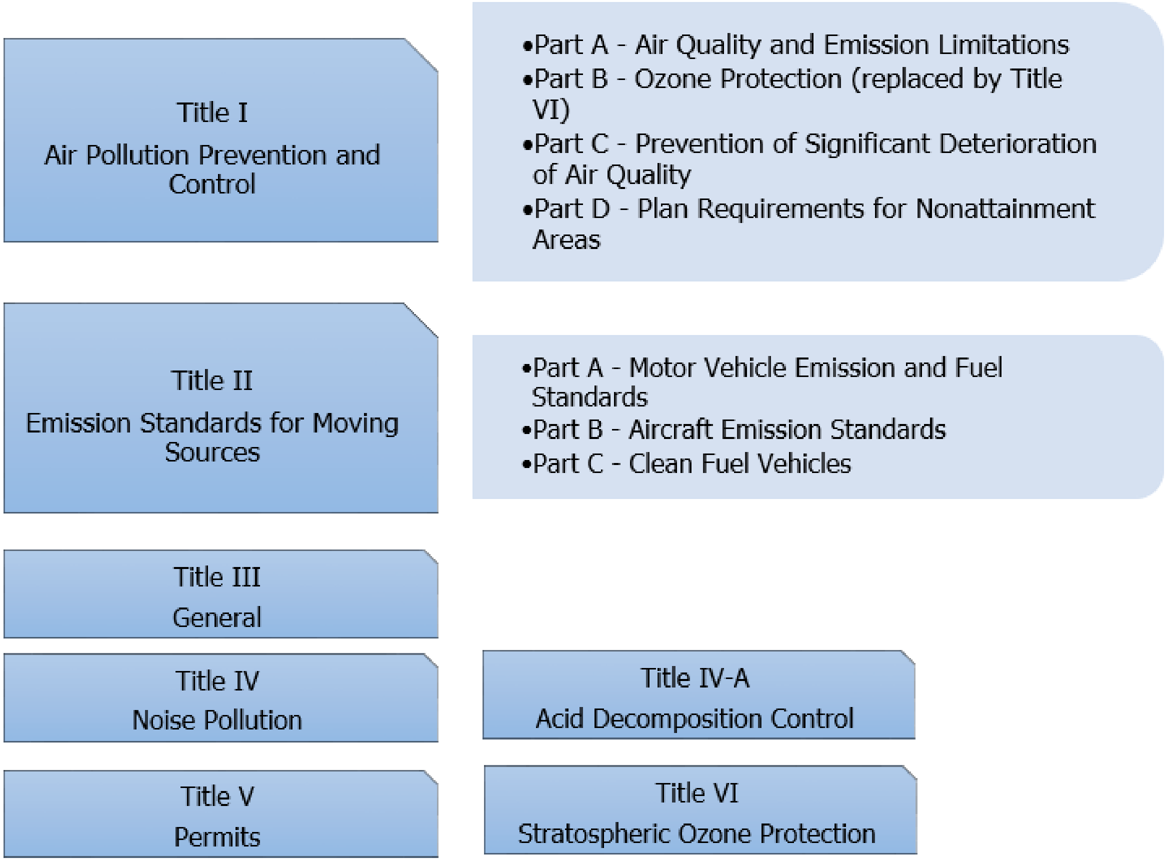


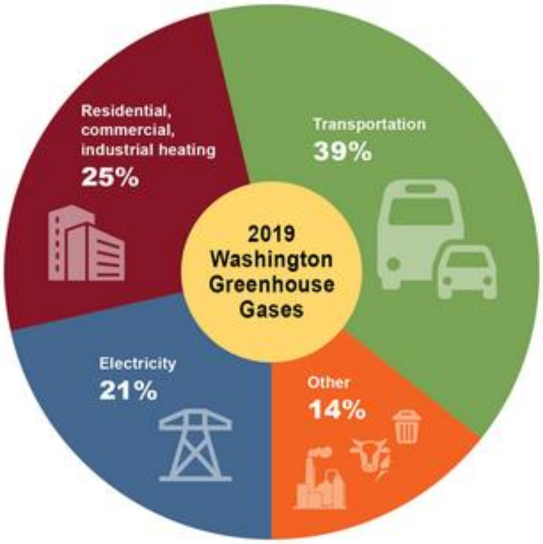
Figure 59 Clean Air Act outline

On top of the above regulatory framework every State reserves its right to promote legislations towards emissions reduction and environmental sustainability, like some States below.

Example regulation cases at a State level

The California Low Carbon Fuel Standard (CA-LCFS) was established in 2009 to reduce GHG emissions in the transportation sector. The policy framework applies a system carbon intensity reduction to put a value on carbon reduction generated from renewable fuels.

Oregon's Clean Fuels Program (CFP) is a market-based program introduced in 2016 and managed by the state's Department of Environmental Quality Commission (DEQ). It focuses on achieving a 37% reduction in the carbon intensity (CI) of transportation fuels used in Oregon by 2035. The 2015 baseline year for the program represents 10% ethanol blended with gasoline and 5% biodiesel blended with diesel. DEQ requires fuel providers to show that the volume and type of fuel they supply for use in Oregon meets the carbon intensity level, or standard, for that year. DEQ gradually lowers the amount of carbon intensity in fuel allowed each year to meet the annual reduction goal. Businesses that create fuels that are cleaner than the annual limit generate credits, while higher carbon intensity fuels create deficits. Credits and deficits are measured in metric tons of greenhouse gas emissions.



2019 Greenhouse Gas Emissions in Washington

Figure 60 Dept. of Ecology - State of Washington

Figure 60 Dept. of Ecology - State of Washington

In 2021, the **Washington** Legislature passed the Clean Fuel Standard with the objective to cut statewide emissions from transportation. From January 2023, the new Clean Fuels Program uses a market approach to incentivize fuel producers to reduce the "carbon intensity" of their products by 20% below 2017 levels by 2034. The requirement to reduce carbon intensity increases over time, making sure all transportation fuels decrease their emissions (https://www.topsoe.com/sustainable-aviation-fuel/saf-legal-framework & "Department of Ecology – State of Washington").

Brazil's & India's commitments to reduce GHGs Emissions

In December 2015 the 21st Conference for the Parties (COP21) of the United Nations Framework Convention on Climate Change (UNFCCC) was held in Paris. Each country that joined the COP21 submitted a plan to reduce domestic emissions of GHGs, called an "Intended Nationally Determined Contribution NDC)". Brazil was one of the countries that joined the Conference and committed to reducing domestic emissions by 37% by 2025 and by 43% by 2030, both compared to 2005 levels. On December 9, 2020, the country confirmed its commitment

Today, Brazil is a global leader in biofuels, and flex-fuel cars provide a large domestic market. More than 90% of cars in Brazil (around 31 million) have flex-fuel engines and the ethanol sector currently accounts for almost 45% of the energy consumed by light vehicles in Brazil. This, together with the mandatory blending of 27% ethanol in petrol, has reduced Brazil's greenhouse gas (GHG) emissions by more than 600 million tons of CO2 over the past 20 years, as this biofuel emits up to 90% less CO2 than fossil fuel.

In addition to its contribution to avoiding global warming, ethanol has also provided a successful experience in the control of pollutant emissions. Its contribution, for example, is well known, so that the city of São Paulo, the fourth most populous in the world, is today one of the metropolises with the lowest level of air pollution. In 2021, the city ranked 1,779th, according to the IQAir list, a platform that monitors and ranks the air quality of municipalities around the globe.

India has committed to generating 50% of its total power from non-fossil fuel sources and reducing carbon emissions by one billion tones by 2030. Several ministries have acknowledged that blending ethanol in conventional fuel is crucial for strengthening energy security by reducing fossil fuel imports and the ethanol program is among the Indian government's priorities. India has even advanced its target of 20% ethanol blending in petrol (E20) by five years to 2025. It is currently the second largest sugar producer in the world, after Brazil and has the opportunity to convert its surplus sugar stocks into ethanol. India has great potential to move forward on an ambitious ethanol program, and the two countries can engage in a fruitful and sound partnership.

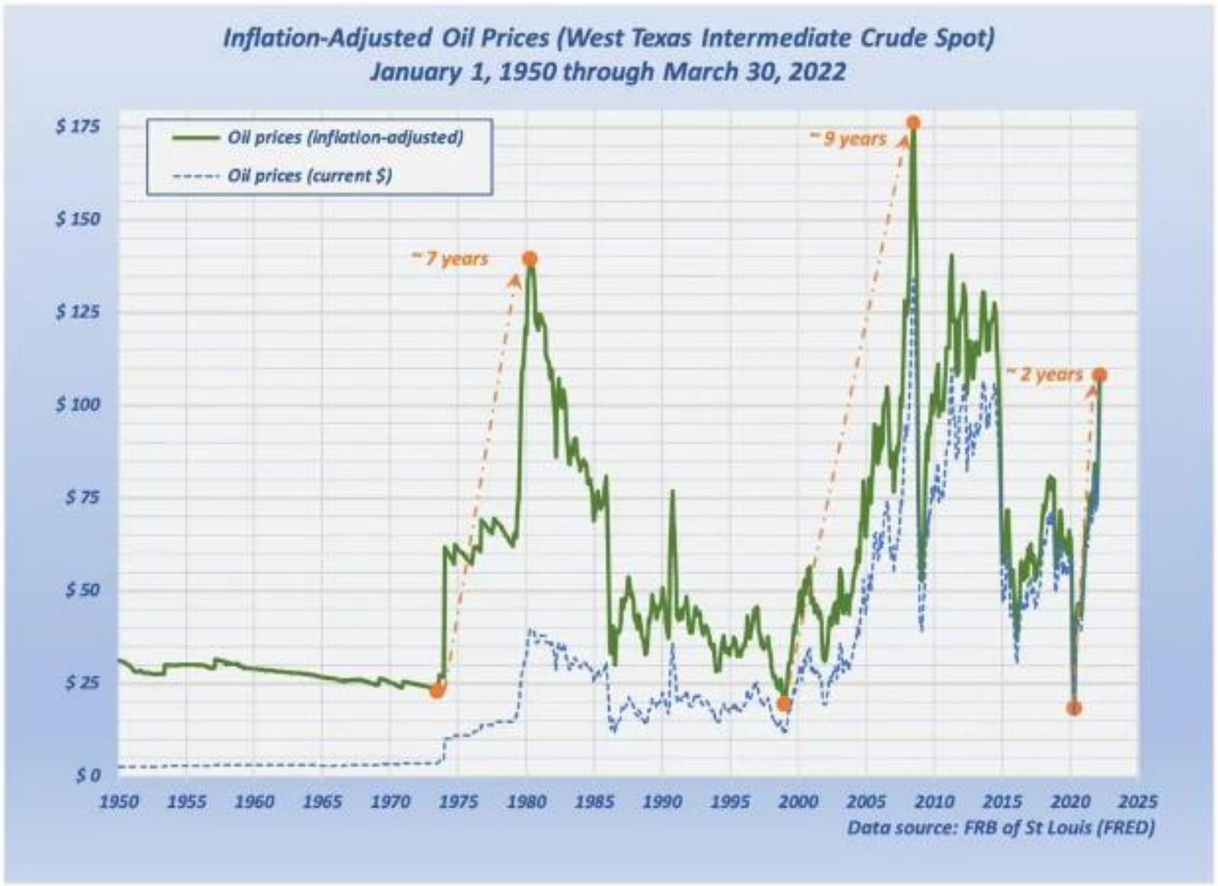
Brazil and India have recently partnered for developing a sustainable, clean energy pathway, within the private sector, for decarbonizing the mobility and the power generation sectors. In April 2022, the Brazilian Sugarcane Industry Association (UNICA) and the Society of Indian Automobile Manufacturers (SIAM) signed a Memorandum of Understanding (MoU) which, among other goals, aims to create a Virtual Center of Excellence (CoE) in bioenergy. The idea is to share knowledge about the use of ethanol and flex-fuel technologies. The CoE will be a knowledge portal – a hub that provides the latest and state-of-the art information on technological advancements, technical standards, regulations, market access, and public policies pertaining to biomass and bioenergy.

Together, India and Brazil can work with other countries who are looking to explore ethanol blending to reduce the carbon footprint of their respective transportation sectors. As two of the world’s biggest developing economies and largest producers of sugarcane, India and Brazil are well-positioned to support the rise of ethanol as a global commodity and pave the way for a thriving international market for ethanol. Given India’s size and geopolitical importance, an ambitious ethanol program on its part will not only help in creating a robust, commoditized market, but also send an important signal to other Asian and sugarcane-producing nations about the feasibility and benefits of such a program.

THOUGHTS FOR FUTURE PERSPECTIVES IN OIL INDUSTRY

Oil is one of the major commodities being traded in huge amount of barrels in the international markets, every single day. For one decade (2005-2014) crude type WTI (West Texas Intermediate) was being traded for over 100 $/bbl (inflation adjusted unit price) and more precisely at the range of 120-140 $/bbl. It has been recorded even nearly to 180$/bbl (2008). Commodities like crude oil are highly dependent not only to the supply and demand principal rule but also on the geopolitical developments around the globe. In the long run the price of basic commodities are highly correlated to the evolution of technology for their extraction and treatment for making them ready-to-use products and to the inflation of the biggest and most robust economies worldwide. The prices are getting higher as the inflation gets higher meaning that the commodities getting liquefied into money. That’s why people holding gold claim that dollars are being measured in ounces and people which “fancy” oil claim that dollars are being measured in oil barrels. Let’s take for example the inflation in US economy. One dollar in 2005 values as much as 1,57 dollars as of today. That means that whatever you could purchase with 1 dollar in 2005, now you need to spend 1,57 dollars.

Figure 61 WTI crude price variation over decades (https://tradingeconomics.com/commodity/crude-oil)



Inflation-adjusted vs nominal oil prices JOHN TOBEY (FRB OF ST LOUIS - FRED)

Figure 62 Inflation adjusted WTI crude unit price fluctuation over time, Federal Bank of St Louis-Fred (Federal Bank of St Louis – Fred)

In times of prosperity everyone concerns about climate impact of human's activities and environmental policies are extremely high in developed countries' agenda. At the same time nobody cares about economy. On the other hand, during recession times in the past, nobody was talking about environmental issues and people used to worry about their economic state of life.

These days there are plenty of individuals and several official country representatives that condemn oil, accuse oil industry for the depreciation of the environment and get in favor of electric vehicles for transportation purposes. But if global economy needs to evolve, societies need to fight inflation by consuming cheap goods. That means that consumables will have been produced cheaply, in terms of energy and any other resources usage.

In addition to that, the energy needs of the world are steadily soaring. And that will be the case as long as the developing countries' appetite for consumables – transportation cars included – and other goods and/or services, like electricity, will be increasing. Undoubtedly, ICE cars production will be much cheaper compared to electric vehicles (PHEV & BEV) in the short/medium term and they will definitely be more appealing to the consumers of emerging countries. The transportation from distant places and handling of goods and resources for generating aforesaid services to people will act supportively to fuel consumption.

At the point we're standing now and for the forthcoming years, there is no large-scale technology in place to offer abundant and robust energy to the world in an economic way but oil.

CONCLUSIONS

In this thesis we strived to exploit deeply the “life expectancy” of fossil fuels for transportation usage, primarily gasoline and diesel auto. Therefore, we went through a short historical overview, we described the two products themselves along with their characteristics, commercial specifications and respective production processes within a state-of-the art refinery complex. We largely focused on the optimization modelling that is used by refinery engineers to optimize the blending stream usage and effectively minimize the production cost of the final products.

In the second part of this thesis we described in detail the universal developments in the ethanol market as a gasoline substitute and in biodiesel and HVO field as substitutes for diesel auto. We presented also the legislation that floodlights the pathway that transportation fuels need to follow and evolve in a more environment friendly and sustainable manner. Under these conditions road fuels will be able to keep up with the new fuel technologies (hydrogen, ammonia, batteries, etc.), which are already on the oil industry’s doorstep and extend their “life” for several decades in the coming future.

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