

Convert naphtha to gasoline with **methaforming**

Convert
semi-regen CRU
for ↑ profit,
↓ emissions

One flexible process.
Many applications.

Standalone
mini-refinery

Process up to
200k tpa FRN
to serve extra
demand

Upgrade
mixed low octane
naphtha streams



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Objective and Limitations

This document provides a general description of Methaforming: a catalytic process of converting naphthas with an alcohol or another oxygenate (co-feed) into gasoline or BTX concentrate.

This process description is provided for a specific illustrative case of processing full range naphtha (FRN) with a boiling range of 35-180°C (95-356°F), jointly with ethanol, into a RON 90 gasoline blendstock.

Methaforming can process a wide variety of feeds, and FRN with ethanol is only one of the many options. This case illustrates the process as a whole.

A version of the Methaforming process where light olefins are processed along the hydrocarbon and alcohol feeds is known as Aroforming. All versions of the Methaforming process are tolerant to wide variations in the hydrocarbon, oxygenate and olefin feeds. Knowing the composition of the available feeds, their prices, and the prices of the potential products, we will be happy to assist you in selecting optimal combinations of the feeds and the process conditions to meet your specific requirements.

The Methaforming process is protected by 39 issued and pending patents in 20 countries.

Process Overview

Methaforming is a catalytic process that makes a motor gasoline or gasoline blendstock by joint processing of two components:

1. Naphtha: straight-run gasoline, gas condensate and other similar types of naphtha feedstocks (main feed), and
2. Ethanol, methanol, other alcohols or ethers, light olefins and their mixtures (co-feed).

The typical products of Methaforming are:

- Gasoline or gasoline blendstock (Methaformate) with standard-compliant sulfur and aromatics content. The yield of Methaformate is 75-92% of the naphtha feed* with 85-95 RON driven by operator economics. The process conditions can be tuned to produce a concentrate of aromatics (benzene-toluene-xylene, BTX) instead of gasoline blendstock.
- Liquefied petroleum gas (LPG) and pure butane, which may be separated from the LPG.
- Hydrogen rich gas (HRG) or simply fuel gas.

The **key features of the Methaforming process** that determine its applicability and economics are:

- **Flexibility** with regard to the qualities of the feedstocks opens up highly profitable opportunities to make valuable products from low value feeds, in some cases amounting to a “waste to energy” operation. See *Feedstocks* for more details.
- **Superior capital and operating efficiency**, especially at 5 000 bpd (200k tpa) or less. The smallest profitable Methaformer operates at about 50 bpd (2k tpa), the largest currently under design is 12k bpd (480k tpa). See *Process Description*.
- **Reduced carbon footprint** and ability to use ethanol as co-feed for gasoline production, giving the operators in certain geographies additional benefits from carbon credits (see *Process Description*).
- Ability to produce standard-compliant RON 90-92 gasoline in a **single unit**, including sulfur and benzene reduction, makes it possible to run a Methaformer as a standalone unit or as a capacity extension in an existing refinery.

The present process description addresses full range naphtha (FRN) and ethanol as typical feeds.

* For the most frequently used naphtha feeds and the share of co-feed (around 25-35% wt.).

Feedstocks

Methaforming can process almost any naphtha fraction into a gasoline blendstock with low benzene which can be blended with other components of the gasoline pool.

Typical feed for the Methaforming process is a combination of two streams:

1. Naphtha, i.e. hydrocarbon fractions with a boiling range of 35-220°C (95-428°F). One can use feeds of various origin (including virgin naphthas, condensate, natural gasoline, processed naphthas) if they comply with the requirements listed in Table 2. The share of this feed stream is usually 70-85% by weight.
2. Oxygen-containing compounds like C₁-C₄... alcohols (including crude alcohols), ethers, byproducts from production of alcohols, C₂-C₄ olefins including those contained in the dry gas from fluidized catalytic cracker (FCC dry gas), or a mixture of these. The share of this feed stream is 15-30% by weight.

Table 1. Sample Material Balance of a Methaformer with Full Range Naphtha as a Feed.

| Feed | | | Product | | |
|--------------------|--------------|--------------|------------------------|--------------|---------------------------------|
| | kg | % by weight | | kg | % by weight |
| Full range naphtha | 1 000 | 79.2 | C5+ Methaformate | 896 | 71.0 (89.6% of naphtha feed) |
| | | | LPG and butane | 259 | 20.5 |
| | | | Hydrogen-rich fuel gas | 6 | 0.5 |
| Ethanol | 262 | 20.8 | Reaction water | 103 | 8.0 |
| Total: | 1 262 | 100.0 | Total: | 1 262 | 100.0 |

Types of Naphtha

The feed requirements are presented here in a condensed form, for the most frequently encountered feeds (condensate, virgin naphtha).

Methaforming has been successfully used to process the following hydrocarbon feeds:

- straight-run gasolines (virgin naphthas), including full range, light, and heavy naphthas,
- gas condensates,
- natural gasoline,
- pyrolysis gasoline,
- raffinates from aromatics extraction units,
- light FCC naphthas (with 20-25% wt. of olefins),
- benzene-rich naphthas (up to 10% vol. of benzene in the feed),
- narrow fractions of C₆-C₇ hydrocarbons (boiling range 60-85°C),
- light naphthas and solvents (up to 30% vol. of C₅ components), including those of synthetic origin (e.g. the products of Fischer-Tropsch process, known as GTL naphtha).

This list of possible naphtha feeds is not exhaustive.

If a feed meets the requirements of Table 2, then it can be a candidate for Methaforming regardless of its origin. A decision regarding non-conventional hydrocarbon feeds may require detailed information on their composition, including various impurities and catalytic poisons. The yields and qualities of the products of Methaforming depend on the qualities of the feeds.

Olefins in the feed increase gasoline yield and octane. Caution needs to be exercised with dienes that may cause coking. Thanks to the inhibitory action of water formed during the conversion of alcohol co-feed, the presence of olefins has a lesser effect on the regeneration cycle of the catalyst than would be expected otherwise.

The presence of sulfur compounds up to 1000 ppm in the feed can be tolerated by the

Methaforming catalyst while reducing the cycle length from 30 to about 20 days. The presence of nitrogen compounds (amines and basic nitrogen compounds like pyridine), fluorine, and organic aldehydes and ketones may lead to temporary poisoning of the catalyst. In general, the feedstock should not have more than trace quantities of alkali or amines. The catalyst activity is recovered by routine in situ regeneration.

If present in the feed, CO and CO₂ do not affect the process.

As an illustration, we discuss the processing of full range naphtha (FRN) as the primary feed for a Methaforming unit, jointly with ethanol.

Typical qualities of popular naphtha feeds are shown in Table 3.

Table 2. General Requirements to the Hydrocarbon (Naphtha) Feed.

| Indicator | Unit | Recommended Value | Critical permissible value | Consequences of exceeding recommended values |
|-------------------------------------|-------------------------|--|-----------------------------|---|
| Sulfur content | mg/kg, ppm wt. | not more than 100 | not more than 500 (1 000) | 100-500 – more frequent regenerations; 500-1000 – additional desulfurization. |
| Fractional composition: | | | | |
| Evaporated at 70°C (158°F) | % vol. | not more than 15 | -- | Lower yields of the gasoline product |
| Final boiling point (FBP) | °C (°F) | not more than 180°C (356°F) | not more than 200°C (392°F) | Higher FBP of the gasoline product; more frequent regenerations |
| Saturated vapor pressure | kPa psi | not more than 80 14.5 | -- | Lower yields of the gasoline product |
| Solvent-washed gum content | mg /100 cm ³ | not more than 5 | -- | Elevated gum content in the product; more frequent regenerations |
| Lead content | mg/L | none | -- | Presence of lead in the product |
| Benzene content | % wt. | 2.0 | -- | Elevated benzene content in the gasoline product |
| Research octane number (RON) | | not less than 56 | -- | Lower octane values of the final product |
| Appearance | | Visually free from undissolved water, sediment, and suspended matter | | |

Table 3. Typical Properties of Naphthas That Were Successfully Processed by Methaforming.

| | Light Virgin Naphtha (LVN), C5/C6 | Heavy Virgin Naphtha (HVN), C6+ | Full Range Naphtha (FRN) | Condensate | Raffinate |
|--------------------------------|-----------------------------------|---------------------------------|--------------------------|---------------------|---------------------|
| Boiling range | 35-85°C (95-185°F) | 74-180°C (165-356°F) | 35-180°C (95-356°F) | 30-220°C (86-428°F) | 35-140°C (95-284°F) |
| Specific Gravity , kg/L | 0.65 | 0.74 | 0.73 | 0.63 | 0.69 |
| n-Paraffins , vol % | 40.6 | 21.6 | 25.8 | 38.1 | 21.5 |
| Isoparaffins , vol.% | 44.7 | 29.0 | 29.9 | 42.6 | 65.0 |
| Olefins , vol. % | 0.0 | 1.69 | 1.20 | 0.4 | 3.2 |
| Naphthenes , vol % | 13.4 | 38.0 | 36.3 | 13.6 | 9.6 |
| Aromatics , vol % | 1.3 | 9.6 | 6.8 | 5.2 | 0.8 |
| Sulfur , wt ppm | 5-60 | 200-500 | 25-500 | 25-600 | 1-5 |

Alcohols and Light Olefin Feeds

Methanol and ethanol are typical oxygenates for the Methaforming process (hence the name). However, the process can also accept mixtures of these and other alcohols, simple ethers, including dimethyl ether, and alcohol-water mixtures as the co-feed. The process can accept methanol and ethanol solutions with up to 50% wt. of water (Table 4). We can also assess the possibility of using industrial byproducts with high methanol or ethanol content as co-feeds to Methaforming process.

Examples of such byproducts that were successfully used in the Methaforming process include the output fractions of the alcohol-making process that are lighter or heavier than the intended product (e.g. ethanol or butanol). Such byproduct co-feeds have the dual advantage of low alternative value and the “waste to energy” aspect which may allow the operator to claim additional environmental credits.

An oxygenate feed may be replaced or combined with light olefins e.g. ethylene, propylene, butylene (Aroforming process). Ethylene contained in the FCC dry gas is a very low cost replacement for purchased alcohols. The FCC dry gas would need to be cleaned up as is typically done before it enters the fuel gas system. If this gas mix is used as a feed, the ethylene and propylene will be reactively extracted in the unit while the other hydrocarbon components of the gas (e.g. hydrogen, methane, ethane) would pass through the unit unreacted.

Table 4. Alcohol co-feed specifications

| | |
|--|-------------|
| Dimethyl ether, wt% | Not limited |
| Water, wt % | < 50 |
| Alkali content calculated as ammonia, ppm wt | < 30 |
| Sulfur content, ppm wt max | < 100 |

Products

Methaforming product streams:

1. The primary product is **Methaformate**, a gasoline blendstock. Its typical qualities are shown in Table 5 below. The Methaformate is stabilized for required RVP.
2. The second product is **hydrogen-rich gas (HRG)**, shown in Table 6. HRG is separated in the 3-phase separator. Due to the low concentration of C₁-C₂ and carbon oxides of <5% wt, H₂ purity of 95-97% vol can be obtained. The HRG can be routed to the existing refinery gas sweetening system.
3. The third product obtained upon stabilization of Methaformate is **LPG** (also shown in Table 6). If needed, it could be routed to an existing Merox treater.

Table 5. Typical Qualities of Methaformate from Full Range Naphtha.

| Indicator | Naphtha Feed | Methaformate |
|---|--------------|--------------|
| Boiling range, % vol. evaporated | °C (°F) | |
| 5 | 50 (122) | 43 (109) |
| 10 | 59 (138) | 51 (124) |
| 50 | 103 (217) | 109 (228) |
| 70 | 118 (244) | 128 (262) |
| 95 | 146 (295) | 171 (340) |
| Final boiling point, °C (°F) | 180 (356) | 215 (419) |
| Saturated vapor pressure SVP, kPA | 89.6 | 62 |
| same, psi | 13.0 | 9.0** |
| Relative Density (Specific Gravity), kg/L | 0.73 | 0.75 |
| RON | 70 | 89.6 |
| n-paraffins, % vol. | 25.8 | 11.9 |
| iso-paraffins, % vol. | 29.9 | 33.1 |
| naphthenes, % vol. | 36.3 | 22.2 |
| olefins, % vol. | 1.2 | 5.2 |
| aromatics, % vol. | 6.8 | 27.0 |
| incl. benzene, % vol. | 0.5 | 0.8 |
| Total sulfur, ppm wt.* | 100 | 10 |

Table 6. Sample composition of LPG and fuel gas (with 100 ppmw of sulfur in the feed).

| Component | Content, % wt. | |
|--------------------------------|----------------|-------------------|
| | LPG | Hydrogen-Rich Gas |
| H ₂ | 0.4 | 10.0 |
| H ₂ O | 0.2 | 1.3 |
| C ₁ -C ₂ | 2.1 | 6.4 |
| C ₃ | 51.8 | 34.3 |
| C ₄ | 42.9 | 29.6 |
| C ₅ + | 2.6 | 18.3 |
| H ₂ S | 0.02 (200 ppm) | 0.09 (900 ppm) |
| Total | 100.0 | 100.0 |

* Indicative values typical for this feed and for the resulting products.

** Data from a specific sample test. Like RON, product RVP is an operator-driven design parameter, set to meet the local regulations and operator priorities.

Process Description

Process Chemistry

Naphthas from different sources vary greatly in their hydrocarbon composition and therefore in the ease of conversion in isomerization and reforming, as well as, in Methaforming. Methaforming will convert most of the normal paraffins, naphthenes and olefins to isoparaffins, and aromatics.

There are numerous chemical reactions that occur during the Methaforming process. Some of these reactions are highlighted here.

Upon contact with the catalyst, alcohol yields a corresponding alkyl radical in a highly exothermic reaction of alcohol dehydration. The heat of this reaction supports the subsequent endothermic dehydrogenation of naphthenes (see diagram below; for simplicity, shown with methanol co-feed).

The alkyl radical from alcohol dehydration can alkylate aromatic groups, e.g. converting most of benzene to toluene, xylene and C9 aromatics (see Table 7), or react with itself to make longer-chain radicals, further converted to higher olefins and aromatics.

Olefins in the feedstock follow a conversion pathway similar to the alcohol. Newly formed aromatics can be further alkylated; paraffins and naphthenes can be further converted to isoparaffins and aromatics.

The content of fused-ring aromatics (e.g. naphthalene) in the product remains below 0.5%.

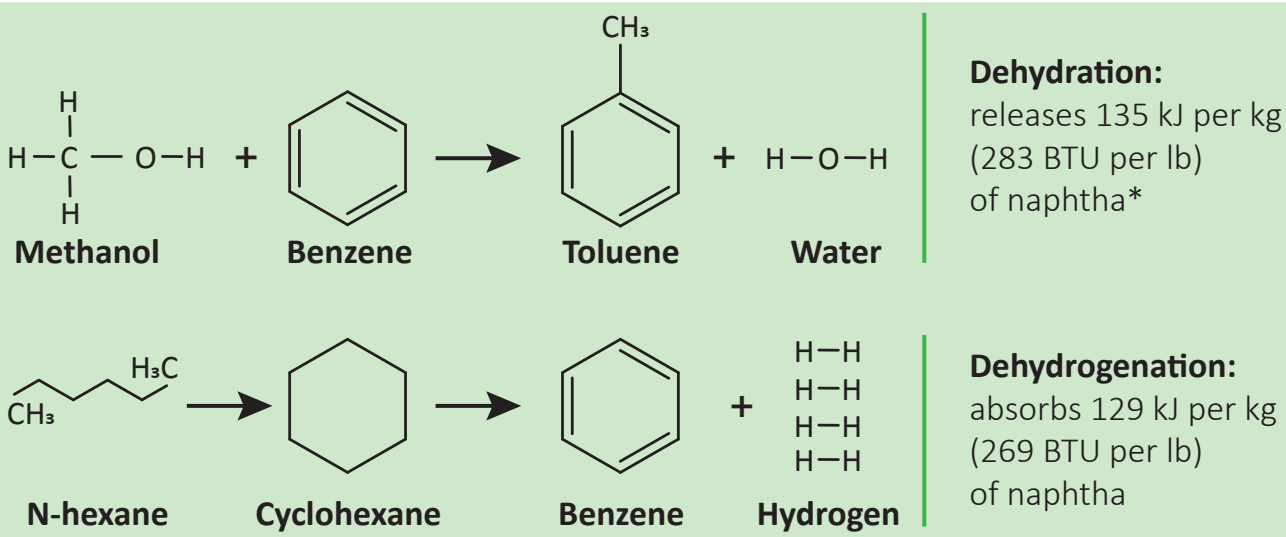
The occurrence of the endo- and exothermic reactions in the same vessel translates into a significant economic and environmental advantage of Methaforming over the traditional methods of naphtha processing due to the reduced reheat duty. For example, with the FRN+ethanol feed combination, the need for fuel gas in Methaforming is 0.58 gCO₂/MJ, or about 1/5 of the corresponding number for the traditional reforming and isomerization suite (3.2 gCO₂/MJ).

The water formed in the alcohol dehydration becomes steam that reduces coke formation on the catalyst, ensuring a longer catalyst cycle.

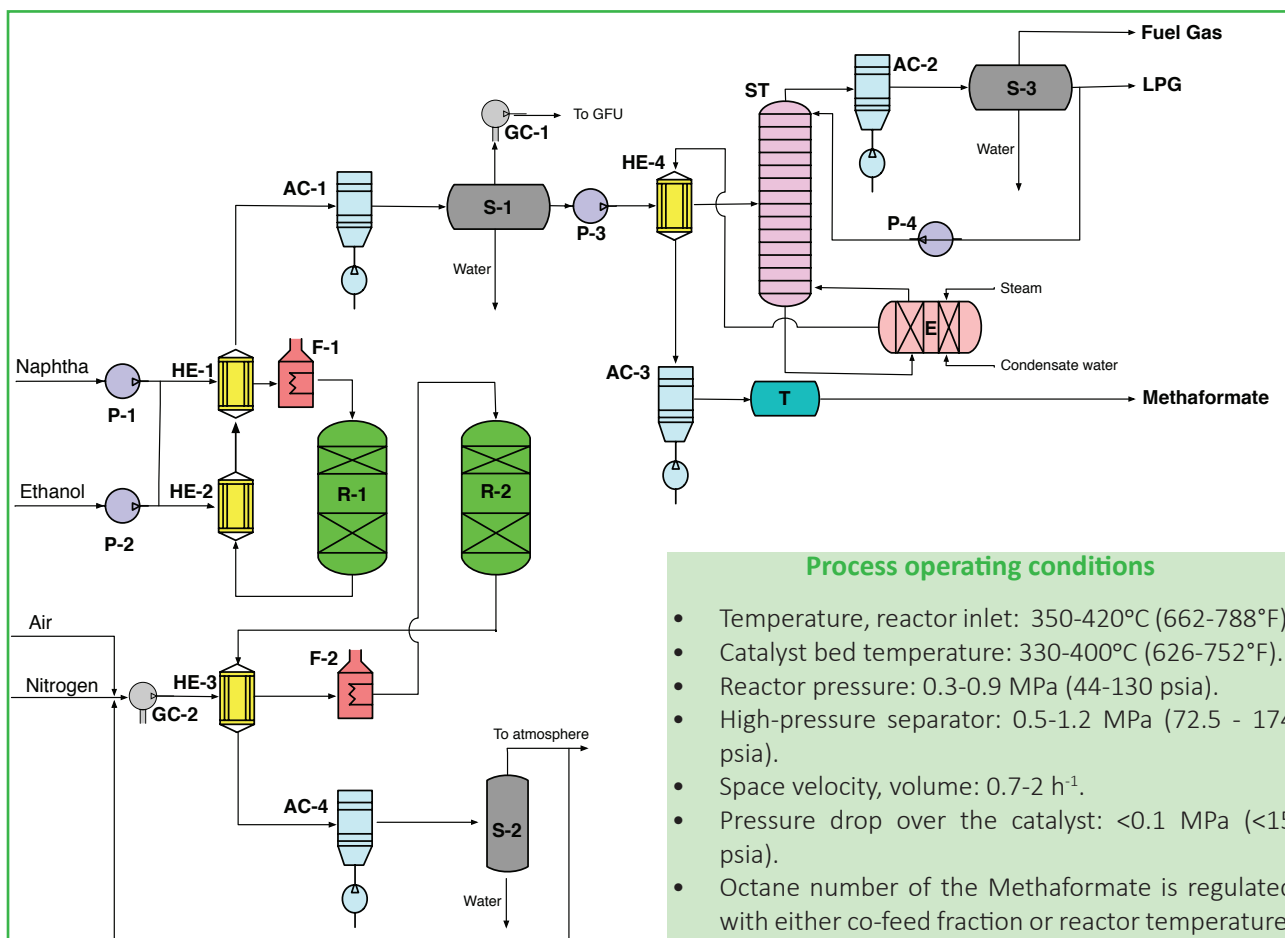
Every step in the pathways is an equilibrium reaction and hence the products of the conversion process will depend on process parameters.

Table 7. Example of The Aromatics Shift.

| % wt. | Naphtha feed | Methaformate |
|---------------|--------------|--------------|
| Benzene | 0.5 | 0.9 |
| Toluene | 1.5 | 5.7 |
| C8 aromatics | 2.5 | 10.7 |
| C9 aromatics | 1.5 | 5.8 |
| C10 aromatics | 0.5 | 2.0 |
| C11 aromatics | 0.2 | 1.1 |
| C12 aromatics | 0.0 | 0.7 |
| Total | 6.7 | 26.9 |



Illustrative Process Flow Diagram and Description



The design provides for the joint processing of feedstock supplied by pump P-1 (naphtha) and by pump P-2 (alcohol).

Heating and vaporization of naphtha and alcohol are performed sequentially in the recuperative heat exchanger HE-1 and furnace F-1.

After heating to 360-430°C (680-806°F), the gaseous feed mixture is fed into reactor R-1 or R-2 which operate alternately (~800 hr on feed and ~50 hours of regeneration). The catalytic process occurs in the reactor converting alcohol and naphtha into Methaformate (gasoline blendstock).

The reaction products at a temperature of 360-430°C (680-806°F) go to the tube side of the alcohol heat exchanger HE-2 and then are cooled further in heat exchanger HE-1, followed by air cooler AC-1. The reaction products cooled to 35°C (95°F) are then separated in a three phase separator S-1. Gas (HRG) from S-1 is fed to the off gas compressor GC-1, then sent offsite.

The liquid phase of the product stream is strati-

fied and decanted in S-1. The aqueous layer is sent to water treating and hydrocarbons go to pump P-3. From there, the hydrocarbon product is preheated in heat exchanger HE-4 and directed to stabilizer ST.

The stabilized Methaformate is withdrawn from the bottom of stabilizer ST. The Methaformate, after cooling in HE-4 and air cooler AC-3 to 45°C (113°F) is routed off-site via product tank T.

The overheads of stabilizer ST are cooled in air cooler AC-2 and fed into the reflux drum S-3, which is a three-phase separator. Uncondensed vapors from the S-3 are routed to the fuel system, and the water is discharged to wastewater treating. The liquid hydrocarbon product is a propane-butane fraction, which goes to pump P-4 and is returned to stabilizer ST as reflux with the balance off-site as LPG.

The diagram and description above are simplified for the ease of comprehension. The actual process flow and equipment for a specific case may differ and include significantly more than is shown above.

The flexibility of Methaforming with respect to the acceptable feeds and operating capacity translates into a wide range of situations where the process can be the optimal choice for an operator. Examples of such applications include:

- **Conversion of a semi-regenerative catalytic reformer or a hydrotreater in front of it into a methaformer.** Such conversion can improve the product yield and – depending on the source of co-feed and local regulations – may allow the operator to claim a financial credit for reducing CO₂ emissions. For example, a conversion of a 860k tpa (20k bpd) semi-regenerative reformer that processes heavy virgin naphtha with ethanol, operates in a jurisdiction where carbon credits can be traded and where the management makes economic decisions based on the US Gulf Coast (USGC) long range prices, would translate into a \$17m additional annual gross profit (\$15m/year yield improvement, and \$2m/year carbon credits*). The value of the carbon credits in this example assumes that the co-feed is carbon-neutral and has no impact on the overall CO₂ emissions of the process**. Given the similarity of process conditions of Methaforming to hydrotreatment, the cost of such a conversion can be estimated at \$15m, translating into a payback period of just under a year.
- **Serving incremental demand for gasoline at 100-5000 bpd (40-200k tpa).** When a refiner sees an opportunity to sell up to 5k bpd (200k tpa) additional gasoline after all debottlenecking opportunities have been exhausted, they should consider using Methaforming. Reforming and isomerization have much higher capital cost per ton or barrel of feed or product and typically require higher operating capacities to justify the investment. Adding a Methaformer in such situation is a capital-efficient solution with a much quicker payback period.
- **Upgrading assorted low-octane naphtha streams.** Many refiners have assorted low-octane naphtha streams that are too small to justify further processing via conventional means. Such streams are either blended into the gasoline pool or sold as low value solvents or petrochemical feeds. Raffinate from the aromatics extraction unit is a classic example of such stream. Methaforming with its tolerance to mixed-molecule feeds can be a very profitable and capital-efficient way of increasing the octane number of such feeds by ~30+ units (e.g. from 60 to 90) with the corresponding step-up in value. The profitability of such upgrade will be even higher if olefins from dry FCC gas are used as co-feed (Aroforming process).
- **Standalone mini-refinery.** An energy entrepreneur with access to economically priced naphtha and/or an appropriate inexpensive co-feed can operate a Methaformer very profitably. For example, processing a condensate or full range naphtha with 100 ppm sulfur content will result in a gasoline product with ~10 ppm sulfur and will require – depending on local conditions and regulations – a relatively inexpensive OSBL setup. We have seen an example where an entrepreneur was able to locate the feeds with such prices that resulted in a gross processing profit from Methaforming of \$400 per ton (~\$45/bbl). Modular Methaformers can be successfully used in such applications; two models can be ordered from us at this time, of 20k tpa (500 bpd) and 6k tpa (150 bpd) naphtha processing capacity.

* Up to \$7.5m/year in California under LCFS rules.

** Different co-feeds can have vastly different carbon “loads” associated with them, depending on their origin and local regulations.

General Specifications and Advantages

General features of the Methaforming process:

- Share of co-feed (alcohols, ethers, olefins) can range from 15 to 50% of the naphtha feed;
- RON of Methaformate: 85-95, can be managed by changing the reactor inlet temperature and/or the ratio of co-feed to naphtha;
- Long cycle length (up to 33 days) and operational life of the catalyst (3-5 years);
- Inexpensive non-precious metal catalyst;
- Similarity to hydrotreatment process, with similar equipment costs, and a possibility for a low-cost revamp of an existing hydrotreater or reformer into a methaformer;
- When feed requirements are observed, the products do not contain components that may lead to gumming;
- Produces hydrogen-rich gas (HRG) for use in other refinery units.

Reactor

The reaction of converting the naphtha together with alcohol and/or olefins to produce high octane gasoline is carried out in a fixed bed, gas phase reactor.

Overall enthalpy change of the reaction mixture during the reaction is small i.e. inlet and outlet temperature are comparable. This is because the dehydration of alcohol is highly exothermic, while the dehydrogenation of naphthenes is highly endothermic.

In general, throughout the catalyst bed, it is desirable for the temperature to remain within $\pm 15^{\circ}\text{C}$ (27°F) of the design value.

A multi-bed reactor with divided input of alcohol to the beds is used to maintain a satisfactory temperature profile.

Service Factor

The process design maximizes operating time. Period of interruption for routine maintenance will be 40 days every 4 years. To achieve this on-stream time, it is necessary to regenerate the catalyst in one reactor while simultaneously processing naphtha with the other reactor.

All critical pumps and compressors, as well as other equipment requiring routine maintenance more often than 1 time in 4 years, will be spared.

Routine operations will be 360 operating days per year (yearly unplanned outages 5 days), representing a 95.9% service factor for a 2-reactor design.

In a Methaformer with only one reactor, service factor will be lower at 76%.

Catalyst

The Methaforming process uses a zeolite catalyst designed for producing high-octane hydrocarbon fractions (gasolines, their components, aromatic hydrocarbon concentrates), from low-octane hydrocarbon fractions, with a co-feed of oxygen-containing compounds (alcohols, ethers), and/or olefins.

The catalyst is in pellet form consisting of a high-silica zeolite of the pentasil group and a binder containing silica and/or alumina. The zeolite is promoted using salts of zinc and rare earth elements.

Table 8. Properties of the Catalyst.

| | |
|---|----------------------------|
| Type of catalyst | proprietary, zeolite-based |
| Loss during calcination at 650°C, wt. % | < 5.0 |
| Bulk density, kg/m ³ | ~ 640 |
| Strength index, kgf/mm diameter | 1.5 |
| Granule diameter, mm | 2.0 – 4.0 |
| Particles <1 mm in diameter, wt% | < 0.5 |

Regeneration of the Catalyst

The regeneration of the catalyst is carried out with nitrogen-air mixture. The nitrogen-air mixture is compressed by compressor GC-2 and heated to 350-550°C (662-1,022°F) in heat exchanger HE-3 and furnace VH-2, and then fed to the reactor R-1 or 2. Exhaust regeneration gas containing nitrogen, carbon dioxide and water is cooled in exchanger HE-3 and air cooler AC-4, wherein a portion of the water condenses and is removed in separator S-2 with the gases discharged into the atmosphere or scrubbed.

The expected cycle time is from 33 days (800 hours) to 17 days (400 hours) minimum, depending on the feed qualities and operating conditions. The amount of coke on the surface of the catalyst at the beginning of the working cycle is 0.3-0.5%wt., and at the end of the cycle, up to 10%.

Regeneration is typically carried out within 2 days, depending on the circulation rate and the amount of coke on the catalyst. The temperature during catalyst regeneration grows from 280 to 510 °C as the oxygen concentration in the circulating nitrogen/air mixture is increased from 1.5% to 18%.

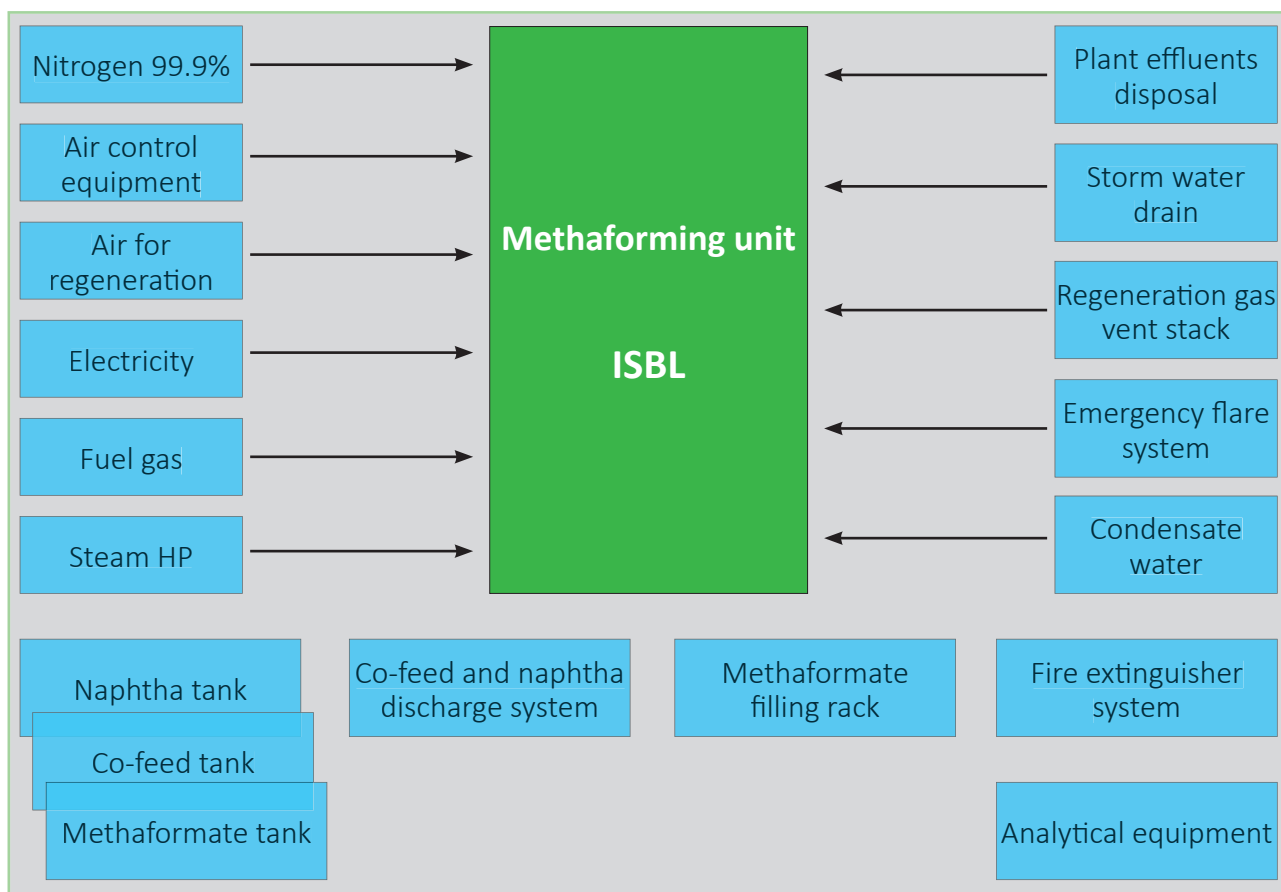
Utility Requirements

The operator will need to have access to standard refinery utilities per the diagram on the facing page.

Approximate requirements for such utilities per unit of naphtha feed are shown in Table 9.

Table 9. Approximate Utility Requirements in the Production Mode.

| | Per 1 m ³ of naphtha feed | Per 1 bbl of naphtha feed |
|--|--------------------------------------|---------------------------|
| Electricity | 8.5 kWh | 1.4 kWh |
| Fuel gas (42 MJ/kg, 18k BTU/lb) | 6.3 kg | 40 k BTU |
| Steam to reboiler of the Stabilizer (1 MPa, 145 psi) | 200 kg | 70 lb |
| Nitrogen | 3 m ³ | 17 scf |



Waste Production and Utilization

Gaseous waste

In general, there are two streams of waste gases:

1. Combustion gases from feed preheater, and
2. Gases from catalyst regeneration (produced in the process of burning coke during regeneration).

The Methaforming process uses significantly less fuel (1/5 to 1/7) than the traditional suite of refining units that is used to process naphtha (hydrotreater and dehexanizer, catalytic reformer and isomerization unit, benzene removal unit).

Solid waste

Under routine operations, no solid waste is generated. Periodically, solid waste is generated when replacing spent catalyst in the reactor. Spent Methaforming catalyst containing traces of naphtha generally may be sent to industrial landfill upon neutralization.

Liquid waste

The water production is 39% wt. of the ethanol co-feed (56% wt. of the methanol co-feed).

The qualities of the effluent water are presented in Table 10 below.

Alcohol content in the produced water is typically nil and always <0.5% wt.

This reaction water from the separator can be directed to a crude desalter or to offsite wastewater treating.

Table 10. Quality of Reaction Water Under Standard Process Conditions.

| | |
|-------------------------|------------|
| Alcohol, ppm | <5 |
| Benzene, ppm | <1 |
| Other hydrocarbons, ppm | 10-50 |
| H ₂ S, mg/L | 0.01-0.10* |

* Depends on the quantity of sulfur in the feed.

How to Benefit from Methaforming

A typical process to bring Methaforming to your site involves the following steps:

1. Feed and economics assessment, product yield modeling.

During this step we will discuss your situation (what feeds do you have available, what are your target products, what other processing units are on site, what utilities are available, what regulatory restrictions apply, etc.), learn about the qualities of your feeds and on the basis of our test library forecast the product yields that you can expect. As a result of this stage you will be able to take a decision whether the expected economics justify continuing with the project. We will not charge you for the work we do at this stage. Once we have all the data from you, it usually takes us a week or less to make the forecast and suggest a range of promising solutions for your situation.

2. Feed testing.

We have an extensive test library which allows us to forecast the product yields that can be expected from processing a wide variety of possible feeds. However, in many cases we recommend testing your specific feed(s) in one of our pilot plants to validate our expectations. Should this be necessary, a typical series of five tests will cost you \$10k, plus the cost of delivering the sample to our lab. If you are interested, you are welcome to witness the testing in person. Duration of the testing depends on how busy our lab is at the time; we usually suggest budgeting about four weeks for this stage.

3. Developing a PTP or basic design package.

We have done design work for modular units of two capacities: 20k tpa (500 bpd) and 6k tpa (150 bpd), and we recommend using them if your feed quantities are close to these numbers or their multiples up to 4 (e.g. if you plan to process about 80k tpa of naphtha, we suggest that you consider using 4 of the 20k tpa units). If your situation calls for using one of these pre-designed units, we will either furnish you with a basic design package or deliver a finished unit as the case may be. Otherwise, at this stage we will deliver to you a preliminary technology package (PTP) that will allow your preferred EPC contractor to design and build a Methaformer. We will discuss the cost and timing of these options with you during the first stage.

For contact information see ngt-synthesis.com

When to Choose Methaforming: an Overview

Naphtha stream is a mix of molecules not suitable for a reformer or an isomerization unit

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Individual fractions of the stream are too small to process separately

- Examples: full range naphtha (FRN) or a mix of raffinate from aromatics extraction and C₅-C₇ stream in quantities of under 200-300k tpa (< 5-7.5k bpd).

Dry gas from an FCC unit is available as a co-feed

- FCC dry gas usually contains ~20% of C₂= and C₃= that would be chemically extracted and converted into products in the Methaforming process.

Non-standard (=cheap) naphtha or other feed, feed qualities vary over time

- Examples: sulfurous naphtha or condensate, byproducts of alcohol production.

Raising new capital is too costly

- CapEx of a new Methaformer is similar to that of a hydrotreater. An existing hydrotreater or reformer can be converted into a Methaformer.

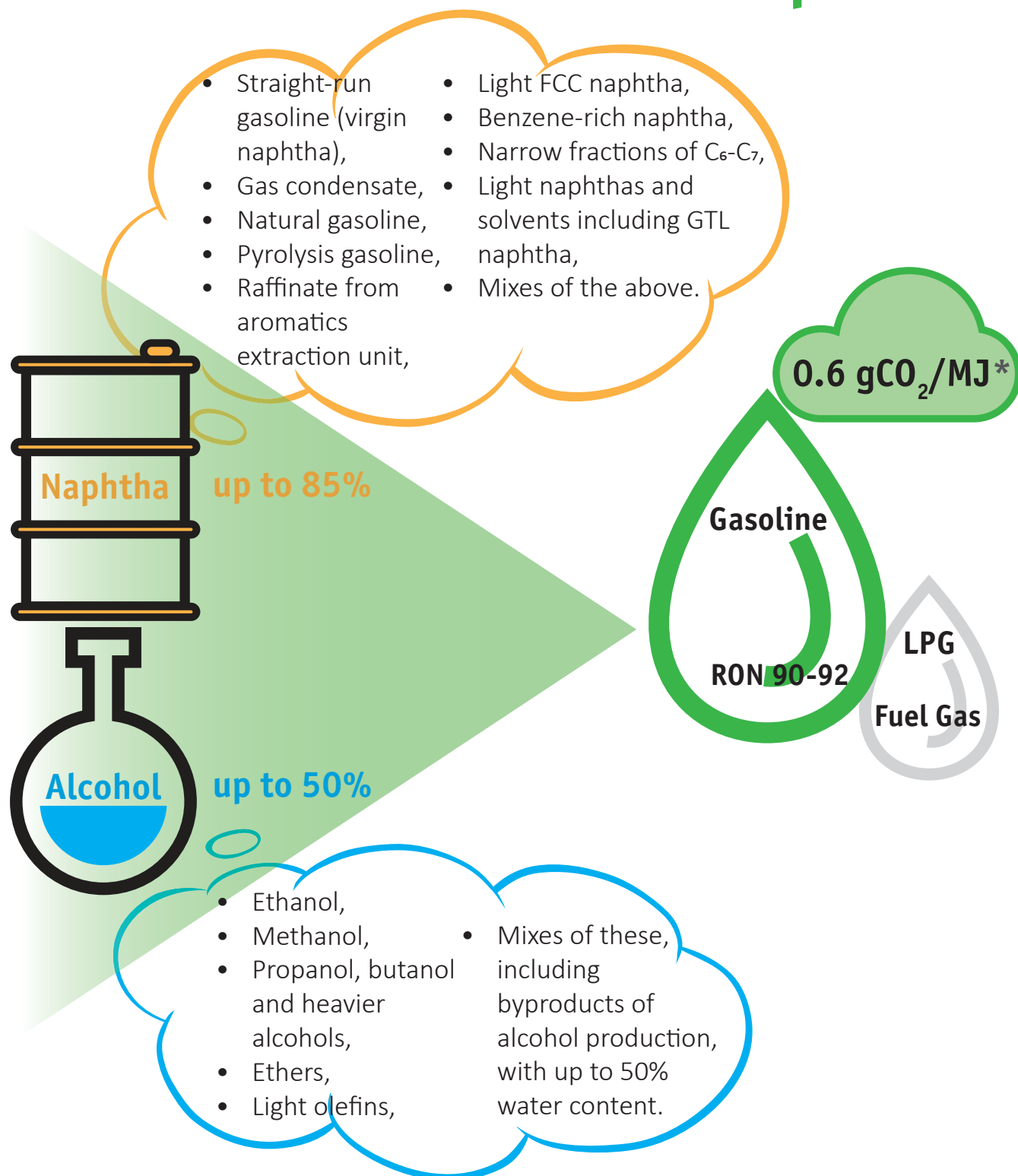
Carbon footprint is important

- Methaforming generates less than 1/5 of the CO₂ emissions of the traditional naphtha processing suite, saving over 100kg CO₂ per ton of product.

* Note to the back cover: compared to 3.2 gCO₂/MJ for traditional naphtha processing.

methaforming

Simple one stage process Tolerant to feed qualities



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