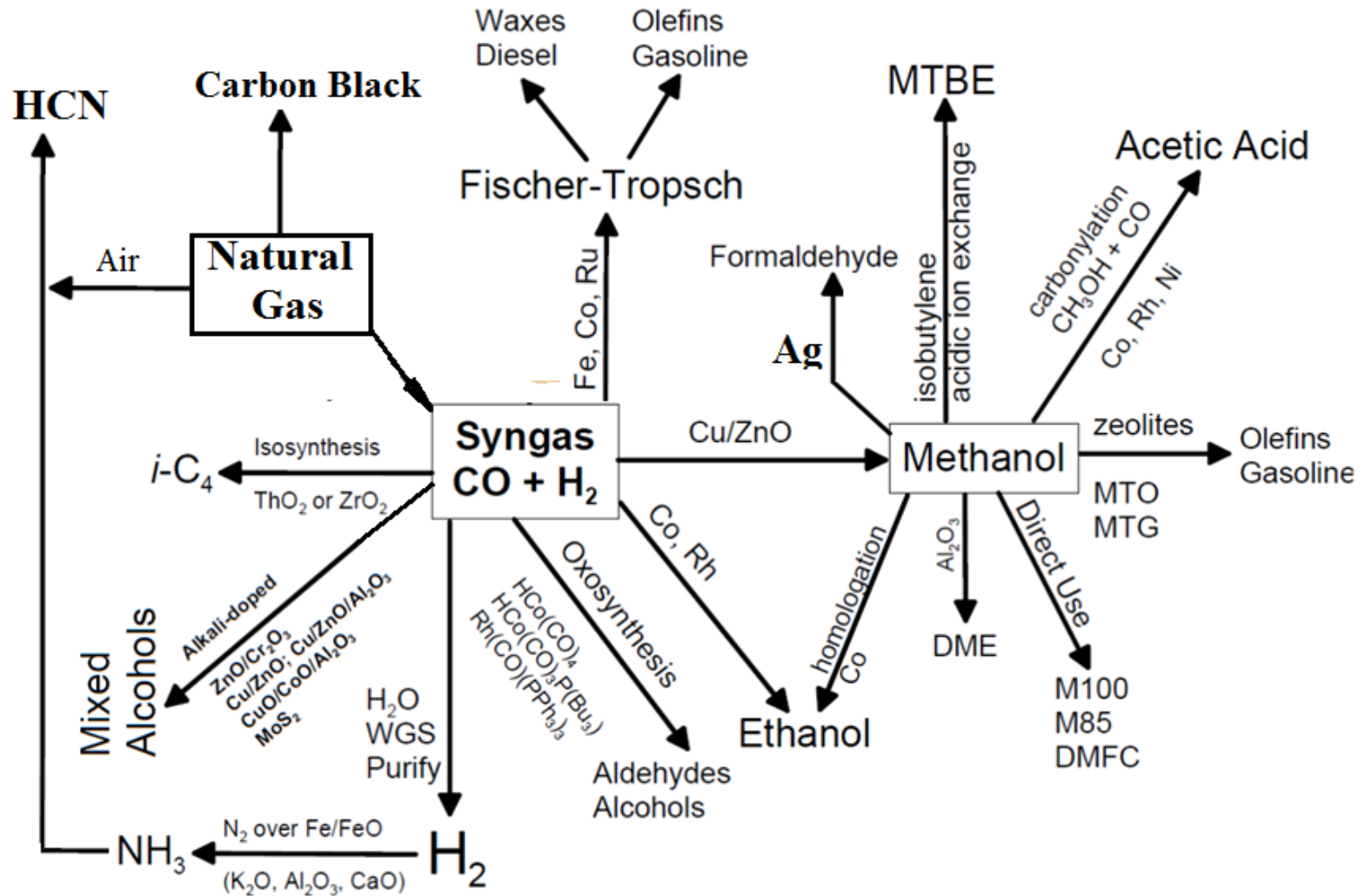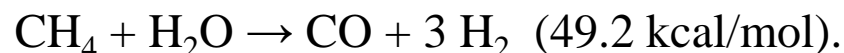# Petrochemical Technology

Chemicals from Natural Gas

# Chemicals from Natural Gas

Hydrogen Production from Natural Gas

1: Reforming: This involves catalytic reaction of methane with steam at temperatures in the range of **760 to 820ºC** according to the following reaction:

$$CH_4 + H_2O \rightarrow CO + 3\ H_2 \quad (49.2 \text{ kcal/mol}).$$

The reaction is endothermic and is carried out by passing the gas through catalyst filled tubes in a furnace. The catalyst is usually in the form of hollow cylindrical rings ranging up to ¾ in. in diameter. It consists of **25-40% Nickel oxide on low-silica refractory base.**

2. Shift Conversion: More steam is added to convert the CO from step 1 to an equivalent amount of hydrogen by the following reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (- 9.6 \text{ kcal/mol}).$$
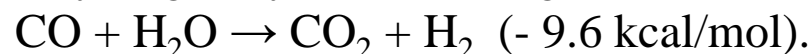
This is an exothermic reaction and is conducted in a fixed-bed catalytic reactor at about **345ºC**. Multiple catalyst bed in one reactor with external cooling between beds are commonly employed to prevent the temperature from getting too high as this would adversely affect the equilibrium conversion. **The catalyst used is a mixture of chromium and iron oxide.**

**3. Gas Purification:** The third step is the removal of CO_2 by absorption in a circulating amine or hot potassium carbonate solution. Several other treating solutions are in use. The treating solution contacts the hydrogen and CO_2 gas in an absorber containing about 24 trays or the equivalent amount of packing. Carbon dioxide is absorbed in the solution which is then sent to still for regeneration.

4. Methanation: In this step, the remaining small quantities of CO_2 and CO are converted to methane by the following reactions:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2 H_2O.$$
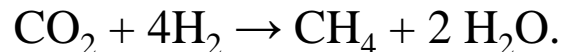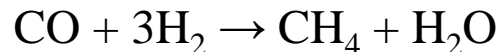
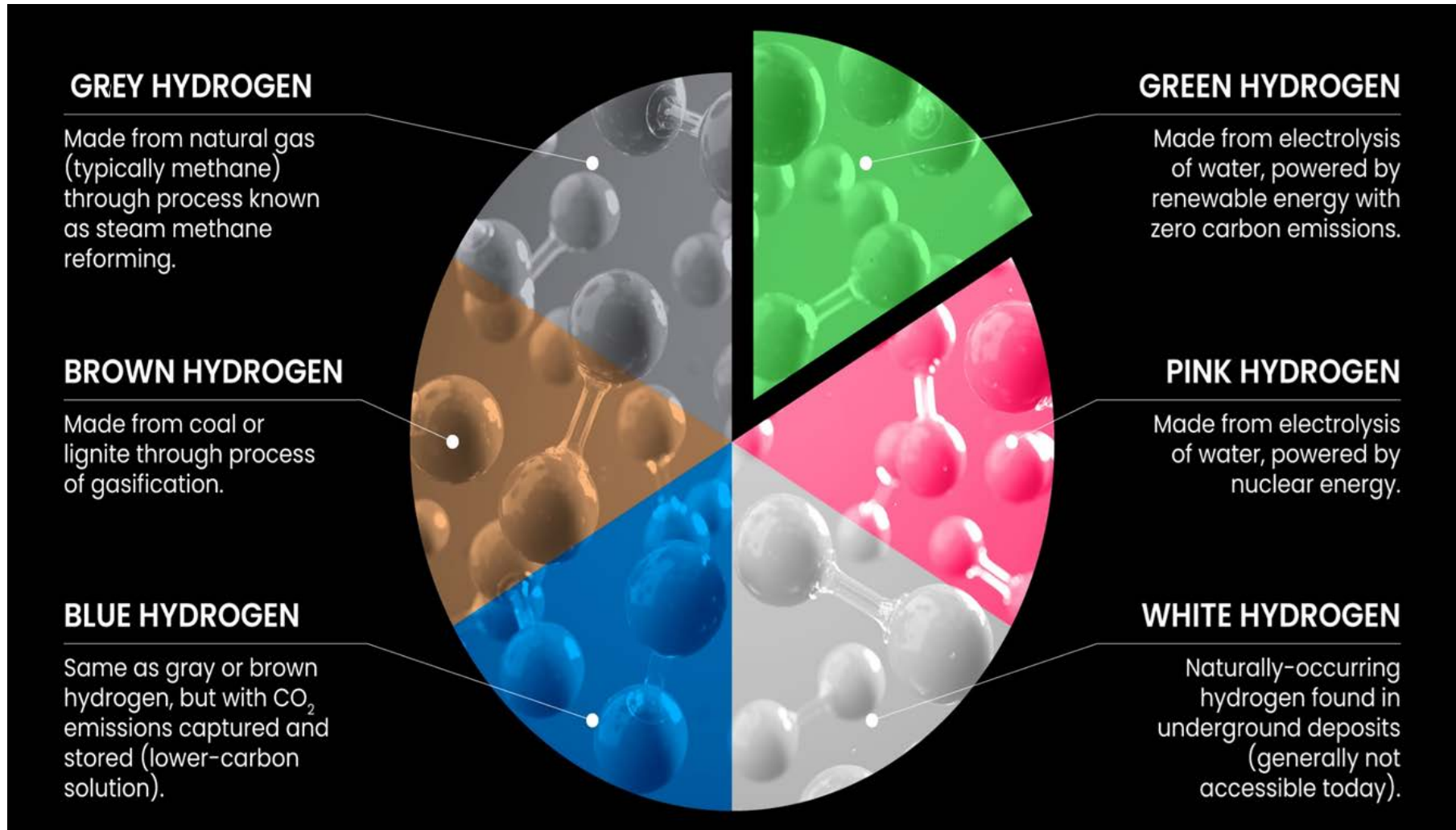This step is also conducted in a fixed bed catalytic reactor at temperatures of about **425ºC.** Both reactions are exothermic and, if the feed concentrations of CO and CO_2 are more than 3%, it is necessary to recycle some of the cool exit gas to dissipate the heat of reaction. **The catalyst contains 10-20% nickel on a refractory base**.
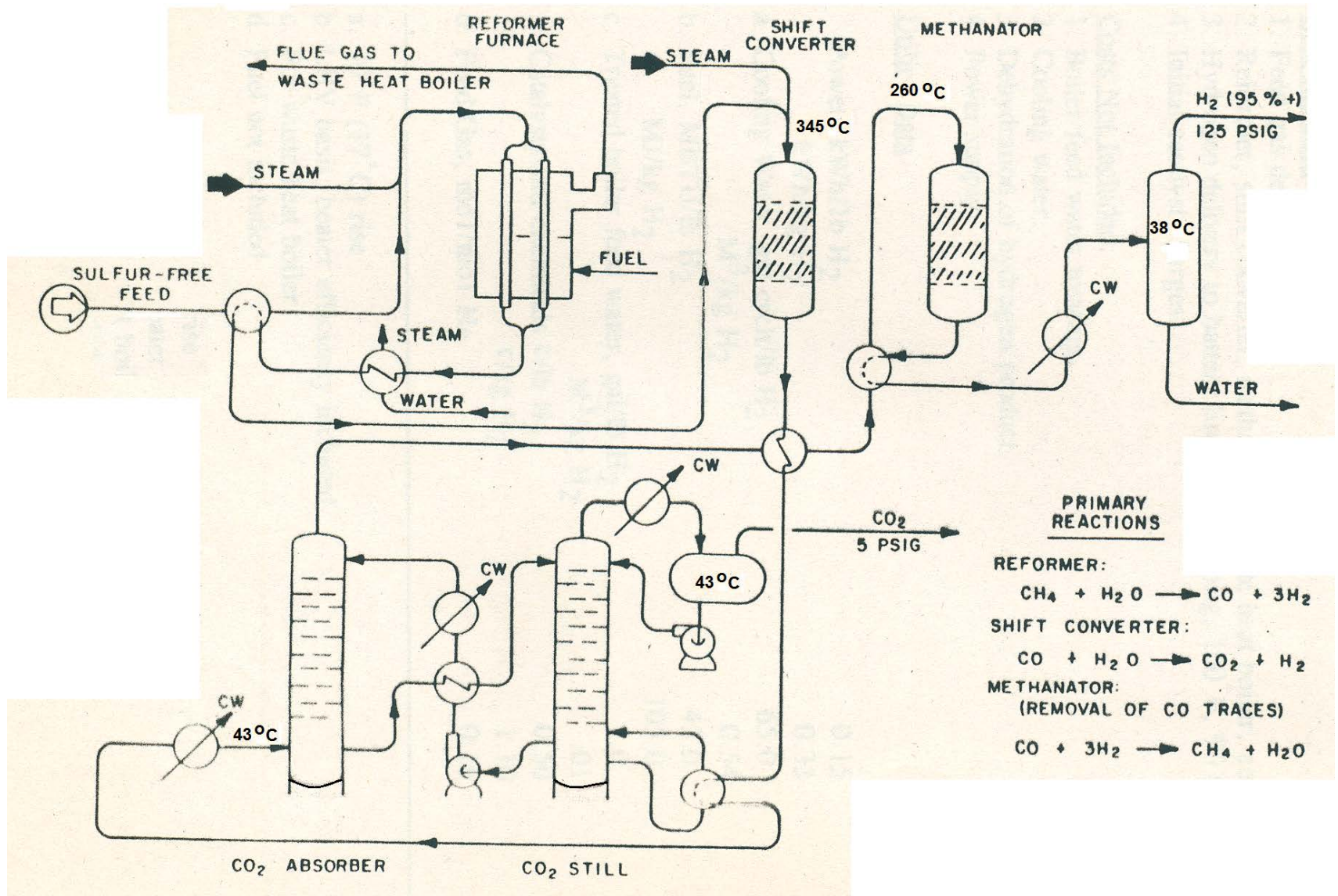
Flowsheet for Production of Hydrogen from Natural Gas

Types of Hydrogen with Colour Codes

GREY HYDROGEN

Made from natural gas (typically methane) through process known as steam methane reforming.

BROWN HYDROGEN

Made from coal or lignite through process of gasification.

BLUE HYDROGEN

Same as gray or brown hydrogen, but with CO_2 emissions captured and stored (lower-carbon solution).

GREEN HYDROGEN

Made from electrolysis of water, powered by renewable energy with zero carbon emissions.

PINK HYDROGEN

Made from electrolysis of water, powered by nuclear energy.

WHITE HYDROGEN

Naturally-occurring hydrogen found in underground deposits (generally not accessible today).

Synthesis Gas (Syngas) Production from Natural Gas (NG) by Autothermal Reforming (ATR)

Reactions:

Reforming reaction:

$CH_4 + H_2O \rightarrow CO + 3H_2$ $\Delta H = 49.2$ kcal/mol

Combustion reactions:

(a) $CH_4 + 2O_2 \rightarrow CO_2 + 2 H_2O$ $\Delta H = -212.8$ kcal/mol

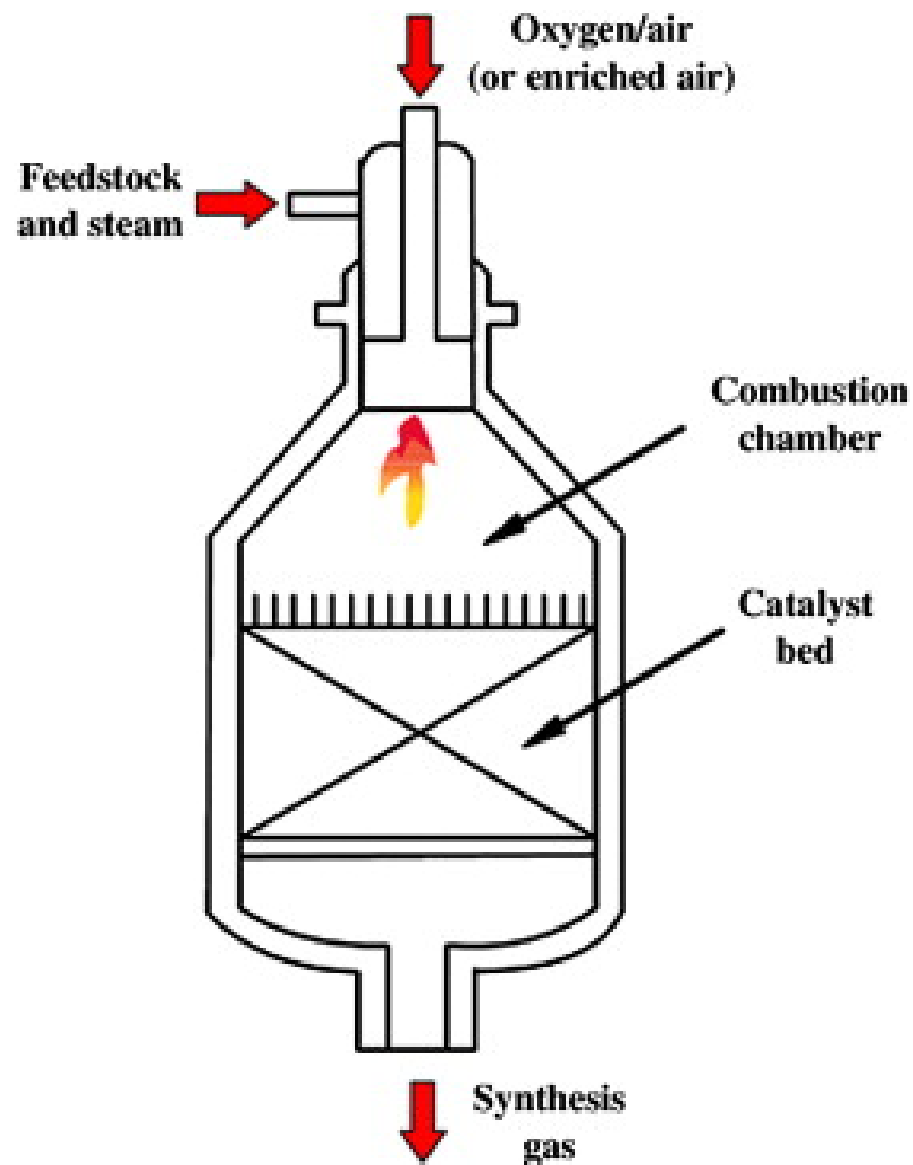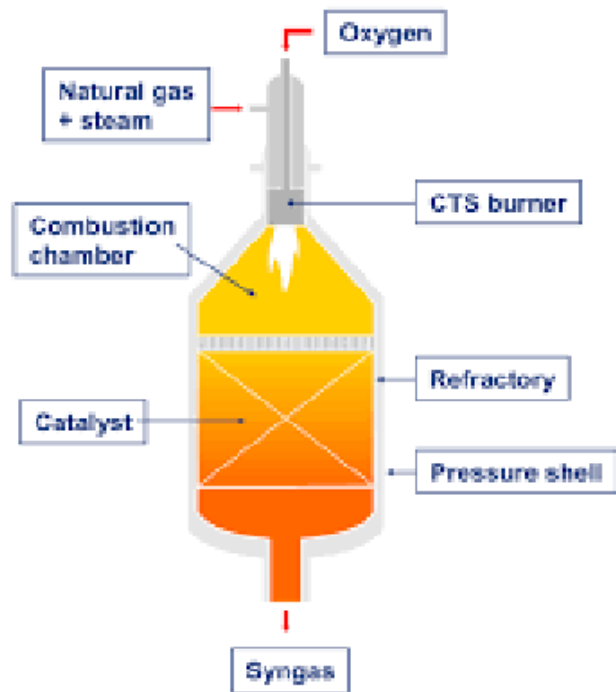(b) $CH_4 + 1.5O_2 \rightarrow CO + 2 H_2O$ $\Delta H = -77.8$ kcal/mol

Reaction Conditions: Temperature, 760-820°C; Pressure, 30-35 atm

Catalyst: Nickel oxide (25-40%) on low silica refractory base

Oxygen/air (or enriched air)

Feedstock and steam

Combustion chamber

Catalyst bed

Synthesis gas

Autothermal Reformer

The autothermal reforming reactor consists of three zones: (1) the burner, where the feed streams are mixed in a turbulent diffusion flame; (2) the combustion zone, where partial oxidation reactions produce a mixture of carbon monoxide and hydrogen; and (3) the catalytic zone, where the gases leaving the combustion zone attain thermodynamic equilibrium. Key elements in the reactor are the burner and the catalyst bed – the burner provides mixing of the feed streams and the natural gas is converted in a turbulent diffusion flame:

$$CH_4 + 3/2\ O_2 \rightarrow CO + 2H_2O$$
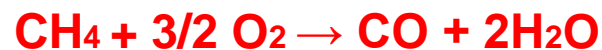
When carbon dioxide is present in the feed, the H_2/CO ratio produced is on the order of 1:1, but when the process employs steam, the H_2/CO ratio produced is 2.5:1.

$$2\ CH_4 + O_2 + CO_2 \rightarrow 3\ H_2 + 3\ CO + H_2O$$
$$4\ CH_4 + O_2 + 2\ H_2O \rightarrow 10\ H_2 + 4\ CO$$

The CTS™ (Cool Tip Swirl) burner is a crucial piece of equipment, and its importance in reformer reliability and availability cannot be underestimated. Good burner performance is characterized by: Short and centralized flame, Low metal temperatures on burner nozzles, Soot-free operation, Easy operation and Long lifetime.
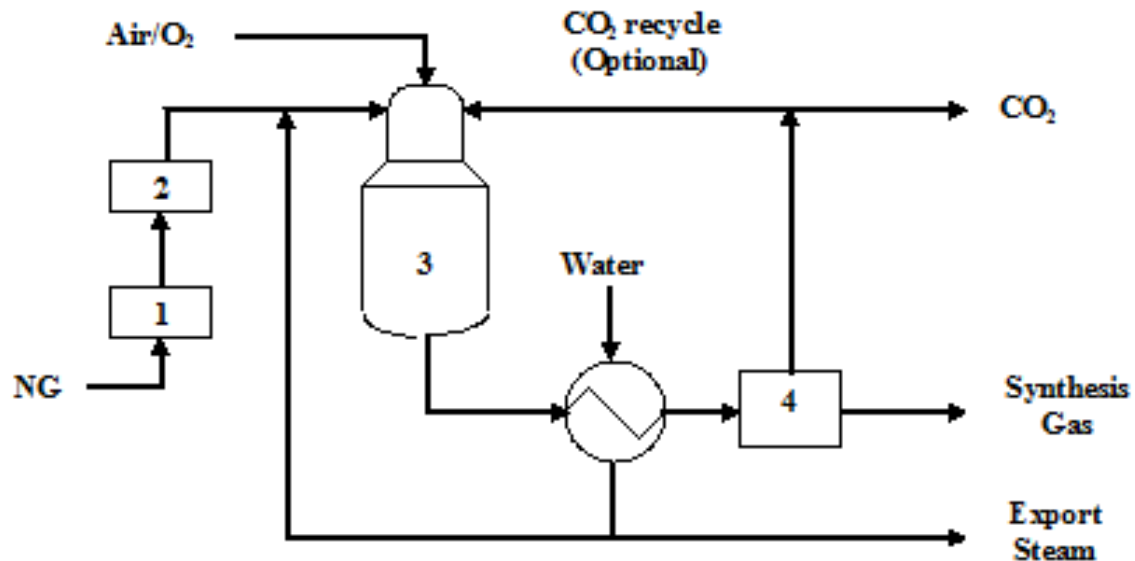
1: Preheater; 2: Desulfurizer; 3: Autothermal Reformer; 4: CO_2 Removal unit

Carbon dioxide can be recycled to adjust the H_2/CO ratio in the product gas. With natural gas as the feedstocks, the H_2/CO ratio in the product gas ranges from about 2.7 (for no CO_2 recycle) to 1.6 (for full CO_2 recycle).

Flow Diagram for Synthesis Gas Production from Natural Gas by Autothermal Reforming
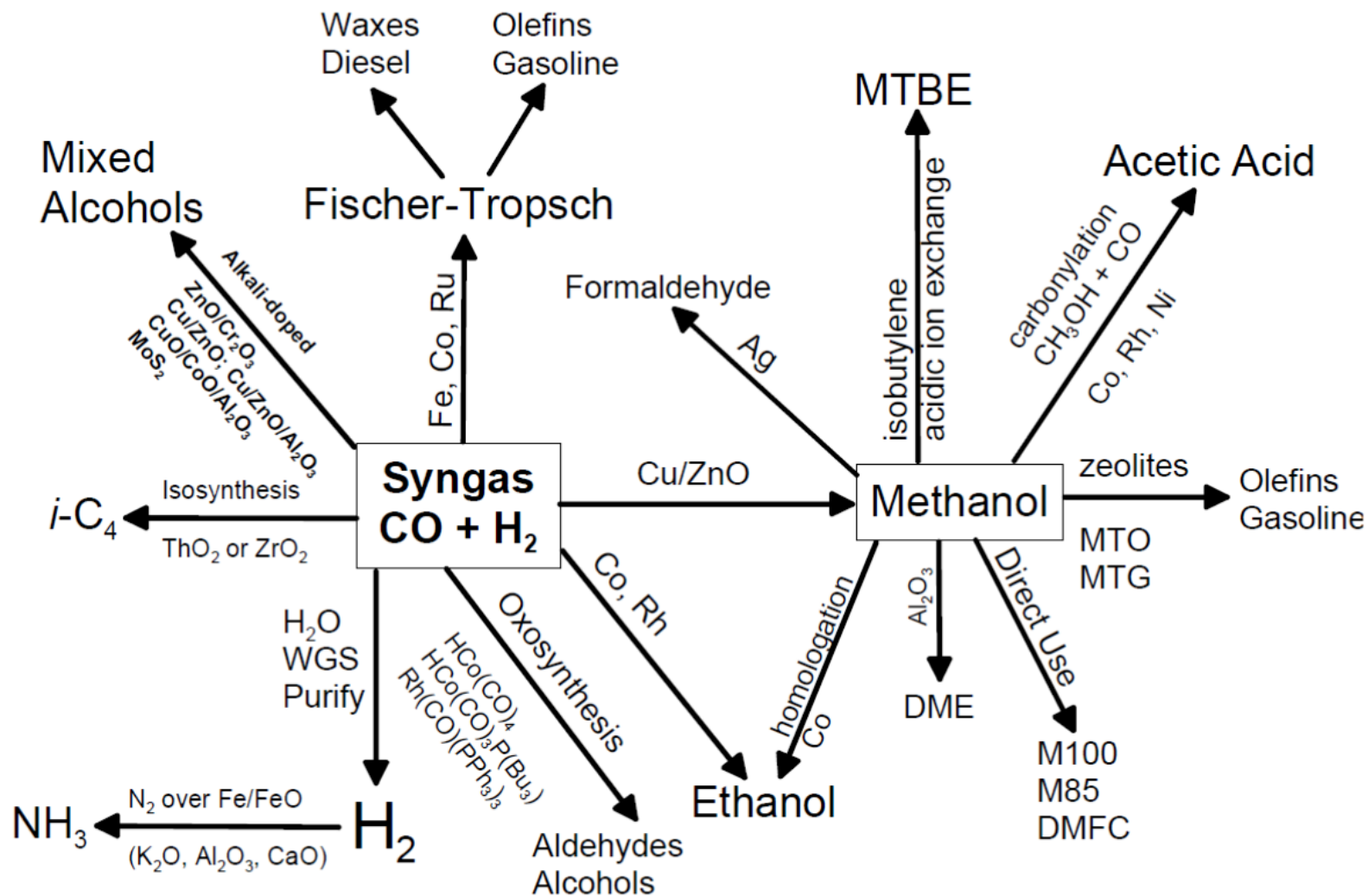
Examples of uses of syngas and methanol

Chemicals from Synthesis Gas

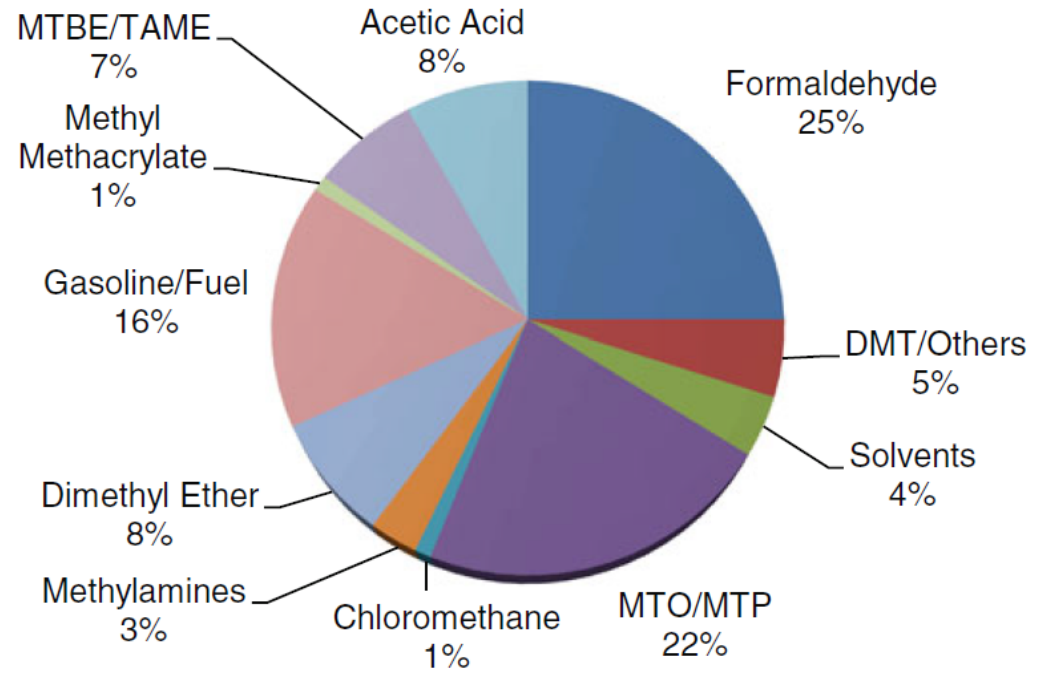| Product	Feedstock	Research reactors	Technology/Process conditions
Methanol	Synthesis gas	Fixed bed, tubular reactor, fluidized bed & slurry bed	ICI technology Fixed bed reactor with quenching Temperature: 240°C Pressure: 50 bar $H_2/CO = 2.0$ Catalyst: Oxides of Zn, Cu & chromium oxide as promoter
Dimethyl ether	Synthesis gas	Fixed bed / slurry bed / liquid phase bubble column	Haldor-Topsoe, Denmark H_2 to CO ratio in syngas: 2.0 Catalyst: γ-alumina and γ-alumina modified with phosphates or titanates Temperature: 290-400°C; Pressure: 80-120 bar $H_2/CO = 2.0$ Feed : Natural gas NKK Corporation, Japan Slurry bed reactor Temperature: 250-320°C; Pressure: 30-50 bar $H_2/CO = 1.0$ Feed : Coal Air Products & Chemicals, USA Bubble column Temperature: ~ 250°C; Pressure: 50 bar $H_2/CO = 2.0$ Feed : Coal, Natural gas etc.
F-T products (Diesel, gasoline, wax etc.)	Synthesis gas	Fixed bed, fluidized bed & slurry bed	Sasol (South Africa) Fluidized bed reactor, 320-360°C and 22 bar H_2 to CO ratio in syngas: 2.0 Catalyst: Iron, cobalt, nickel and ruthenium metal based

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Chemicals from Methanol

Product	Feedstock	Research reactors	Technology/Process conditions
Synthetic Gasoline	Methanol	Fixed bed, fluidized bed	Mobil technology (MTG plant, New Zealand) Fluidized bed reactor, 360-415°C and 22 bar Catalyst: ZSM-5
Olefins	Methanol	Fixed bed, fluidized bed Fluidized	Mobil technology (MTO plant, New Zealand) Reactor: Fluidized bed reactor Catalyst: ZSM-5 Temperature: 470-515 °C Pressure: 3.0-4.5 bar UOP Process SAPO-34 catalyst
HCHO	Methanol	Fixed bed	Ag- or Cu-gauge Temperature: 450-600°C; Pressure: 1 atm. MeOH/Air ratio: 0.3-0.5
CH$_3$COOH	Methanol	CSTR	Monsanto Process Rhodium catalyst promoted with iodine; 180°C, 30-60bar Cativa Process Very similar to the Monsanto Process Iridium-based catalyst Advantages are higher stability of the catalyst, lower reaction rates, less liquid by-products.

Syngas to Methanol

Global Production: 111 MMTPA

Methanol is a key product in the chemical industry. It is mainly used for producing other chemicals such as formaldehyde, acetic acid and plastics. **Around 111 million tonnes (MMT) are produced per annum**, nearly all of which is produced from fossil fuels (either natural gas or coal). The global methanol market size was **USD 30.9 billion** in 2023 and is projected to reach USD 38 billion by 2028. The driving factors for Methanol market is its growing demand from automotive industry.

Pie chart: MTBE/TAME 7%, Methyl Methacrylate 1%, Acetic Acid 8%, Formaldehyde 25%, DMT/Others 5%, Solvents 4%, MTO/MTP 22%, Chloromethane 1%, Methylamines 3%, Dimethyl Ether 8%, Gasoline/Fuel 16%

Methanol Demands and End Uses

DMT: dimethyl terephthalate, MTBE/TAME: methyl tert-butyl ether/tert-amyl methyl ether, MTO: methanol-to-olefins, MTP: methanol-to-propylene

Syngas to Methanol

The transformation of synthesis gas to methyl alcohol is a process of major industrial importance. From the point of view of hydrocarbon chemistry, the significance of the process is the subsequent conversion of methanol to hydrocarbon (thus allowing F-T chemistry to become more selective).

Reaction:

$$CO + 2\,H_2 \Leftrightarrow CH_3OH \quad \Delta H = -21.7 \text{ kcal/mol}$$

An industrial process to produce methanol from carbon monoxide and hydrogen was developed by BASF in 1923 using a Zinc oxide – Chromia catalyst. Since this catalyst exhibited low specific activity, high temperature was required. The low methanol concentration at this high temperature was compensated by using high pressures. This so-called high-pressure process was operated typically at 200 atm and 350^oC.

The high-pressure process was superseded in the 1960s by the ICI low-pressure process after introducing Cu-ZnO-based catalysts. Conditions applied in this process are 50-100 atm and 220-250^oC.

A similar process was developed by Lurgi employing a CuO-ZnO catalyst. Since Cu-based catalysts are sensitive to sulfur and chlorine in the feed, a precondition for their industrial application is the use of high-purity synthesis gas prepared from methane.

The Cu-ZnO binary catalyst has been known to exhibit high activity in methanol formation at low temperature, but fast deactivation prevented commercialization. The addition of a third component, however, resulted in stable catalyst activity. The third component is either Al_2O_3 or Cr_2O_3.

The primary functions of the non-copper components are to enhance dispersion of copper, and to maintain the active phase in a stable dispersion and with suitable physical strength. Cu-ZnO-Al_2O_3 and Cu-ZnO-Cr_2O_3 are usually the most important industrial catalysts, prepared by co-precipitation.
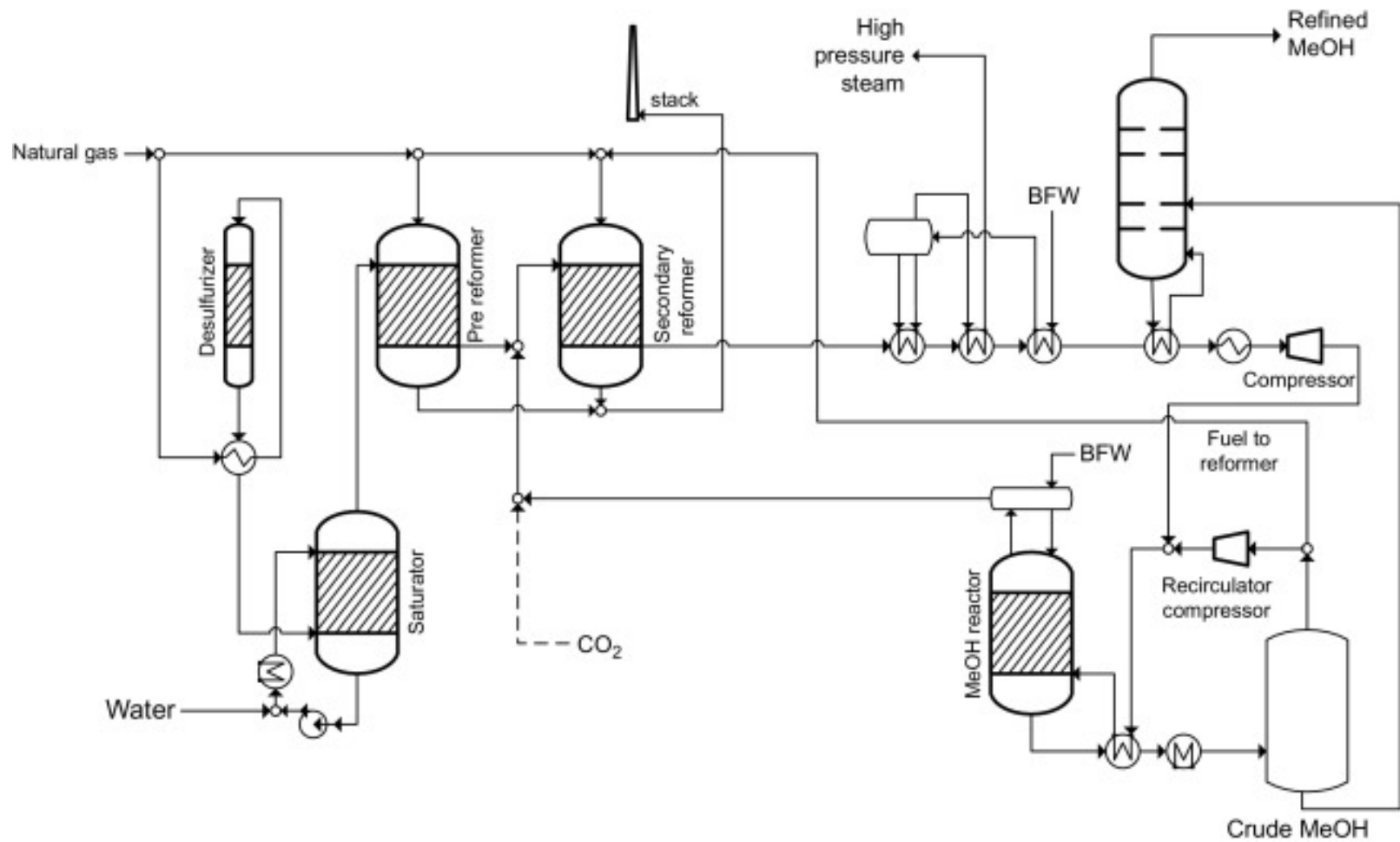
A significant advance was made when a two-stage precipitation was suggested in which $ZnAl_2O_3$, a crystalline zinc-aluminate spinel was prepared prior to the main precipitation of Cu-Zn species. This alteration resulted in an increase in catalyst stability for long-term performance with respect to deactivation. Catalyst lifetimes industrially are typically two years.
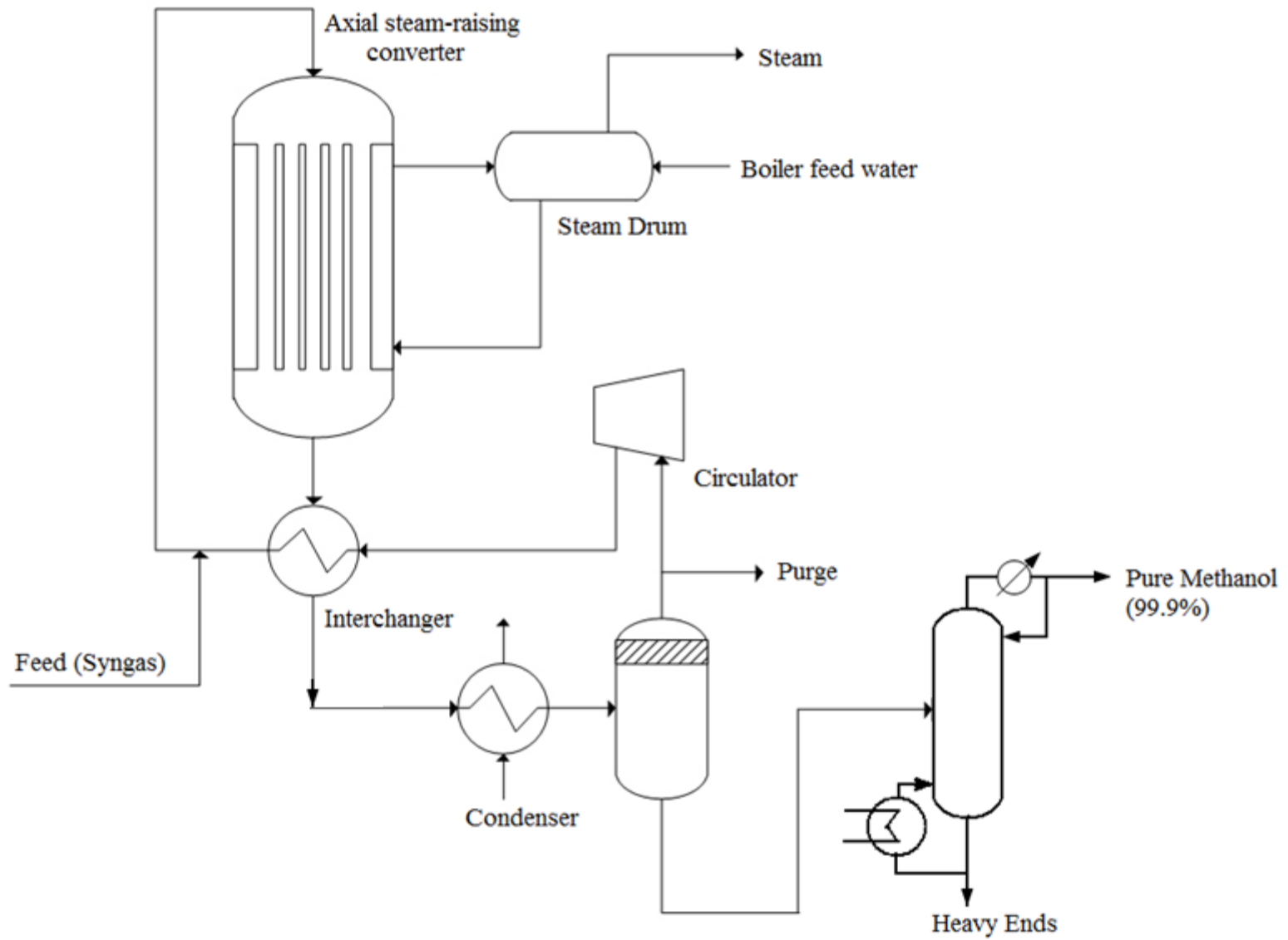
At present, the low-pressure technology dominates the worldwide production of methanol.

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The low-pressure copper catalysts are very selective for the synthesis of methanol. Under industrial conditions on Cu-ZnO-Al$_2$O$_3$ catalyst, the selectivity is typically greater than 99%. The impurities formed include hydrocarbons, higher alcohols, ethers, ketones and esters. These as well as any water formed can easily be removed by distillation to give very pure methanol.

Metal composition of catalysts provided by different manufacturers

Manufacturer	Cu wt%	Zn wt%	Al wt%	Other (wt%)
IFP	45-70	15-35	4-20	Zr (2-18)
ICI	20-35	15-50	4-20	Mg
BASF	38.5	48.8	12.9	
Shell	71	24		Rare Earth oxide (5)
Sud Chemie	65	22	12	
Dupont	50	19	31	
United Catalysts	62	21	17	
Haldor Topsoe MK-121	>55	21-25	8-10	

Axial steam-raising converter

Steam

Boiler feed water

Steam Drum

Circulator

Interchanger

Purge

Feed (Syngas)

Condenser

Pure Methanol (99.9%)

Heavy Ends

Gas-to-Liquid (GTL) Technologies

MTG Process

Fischer-Tropsch Synthesis

Routes for Synthetic Transportation Fuel

Coal
Natural Gas
BioMass

SynGas Generation

Steam

Fischer Tropsch (LT) → **Refining** → **Naphtha & Diesel**

CO$_2$ & Water

Methanol Generation → **Methanol to Gasoline** → **Gasoline**
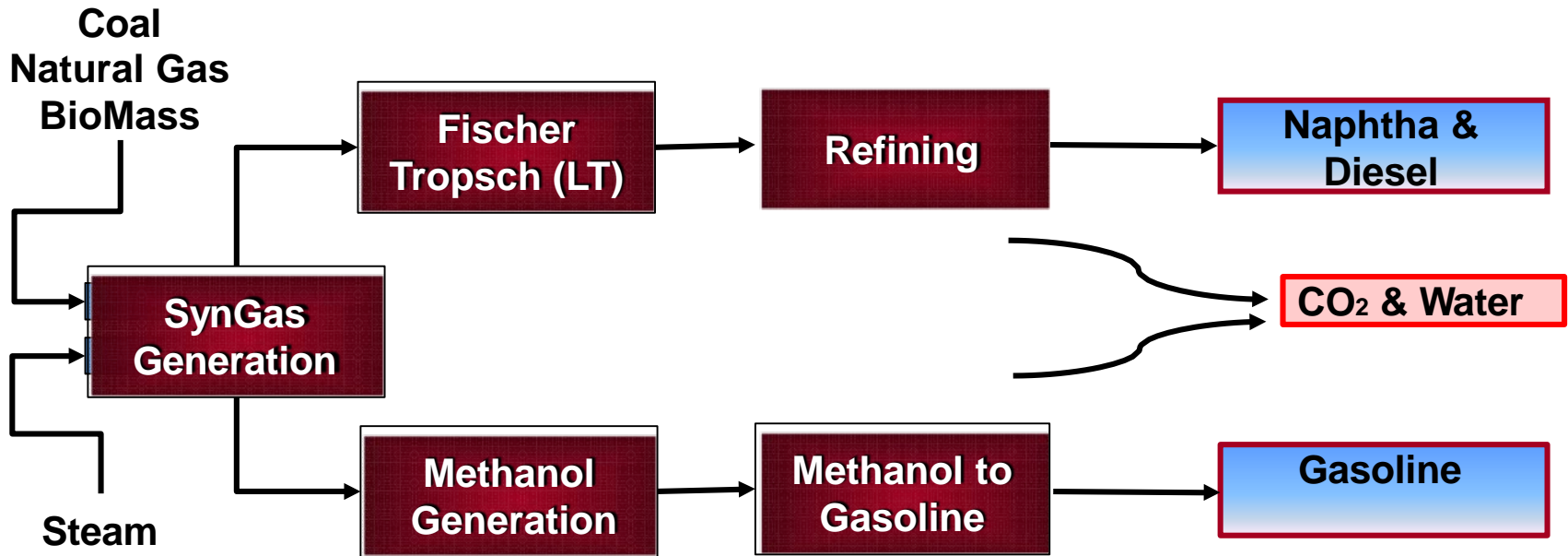
- **Both are 3 Step Process**
- **Thermal efficiencies are essentially governed by initial C/H ratios...Fuels are ~C/H$_2$**
    - **Coal is CH to Fuels plus CO$_2$**
    - **Natural gas is CH$_4$ to Fuels plus H$_2$O**

Both the MTG and Fisher-Tropsch processes convert coal/NG into synthesis gas as an intermediary before producing the final products. However, their respective product slates are very different.

The Fisher-Tropsch process produces a broad spectrum of straight-chain paraffinic hydrocarbon which requires upgrading to produce finished products such as gasoline, jet fuel, diesel fuel, and lube base stocks. Due to the complexity of the product distribution, the economic justification for further upgrading/ processing of all the products recommends for large scale projects (e.g. 50-80K BPD.)

MTG, in contrast, selectively converts methanol to high quality gasoline with virtually no sulfur and low benzene which can be sold as it is or blended in the refinery gasoline pool. About 90% of the hydrocarbon in methanol is converted to gasoline as the single liquid product, with the remainder primarily LPG.

Mobil Technology (Mobil's MTG Process)

Fixed/Fluidized bed reactor, 360-415°C and 22 bar, Catalyst: ZSM-5

Reference:

Methanol to Gasoline: Production of Clean Gasoline from Coal

ExxonMobil *Research and Engineering*

Methanol to Gasoline Chemistry

$$2\ CH_3OH \rightleftharpoons CH_3OCH_3\ +\ H_2O$$

Methanol   Di-methyl Ether

$$CH_3OH,\ CH_3OCH_3 \rightarrow \text{Light Olefins} + H_2O$$

Methanol, Di-methyl Ether

$$\text{Light Olefins} \rightarrow C_5+\ \text{Olefins}$$

$$C_5+\ \text{Olefins} \rightarrow \begin{matrix} \text{Paraffins} \\ \text{Naphthenes} \\ \text{Aromatics} \end{matrix} \Big\rangle \ \text{Gasoline}$$

Overall exothermic reaction, ΔH = - 55.68 kJ/mol

MTG Yields and Properties/Composition

MTG GASOLINE YIELDS		
	Percent of Feed	**Percent of Hydrocarbon Product**
Gas	1%	**2%**
LPG	5%	**11%**
Gasoline	38%	**87%**
H_2O	56%	**-**

MTG GASOLINE PROPERTIES/COMPOSITION	
Octane, RON	**92**
Octane, MON	**82**
(R+M)/2	**87**
Paraffins, vol%	**53**
Olefins, vol%	**12**
Naphthenes, vol%	**9**
Aromatics, vol%	**26**
Benzene, vol%	**0.3**
Sulfur	**nil**

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ExxonMobil MTG Process:
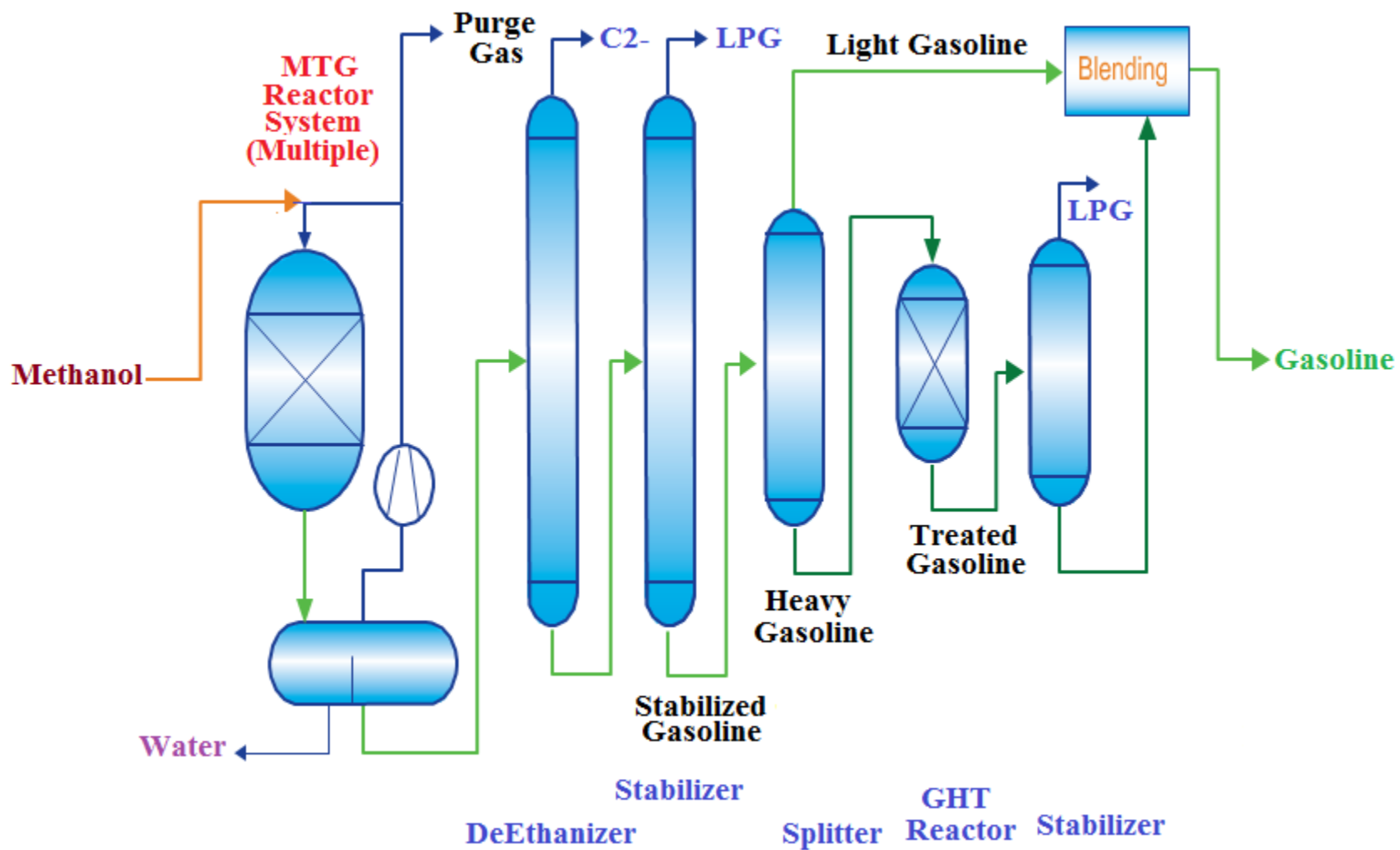## MTG Reactor Section

- Methanol is vaporized by heat from the MTG reaction and fed into a DME reactor

- DME reactor effluent is mixed with recycle gas & fed to the MTG reactors

- Recycle gas controls reactor temperatures

- MTG reactor effluent is cooled by the methanol feed, recycle gas & air or water

- Condensed effluent is separated into gasoline, water and gas

- Raw gasoline is pumped to a recovery section

Basic MTG Process Flow

MeOH

DME

MTG

Raw Gasoline To Recovery Section

Water
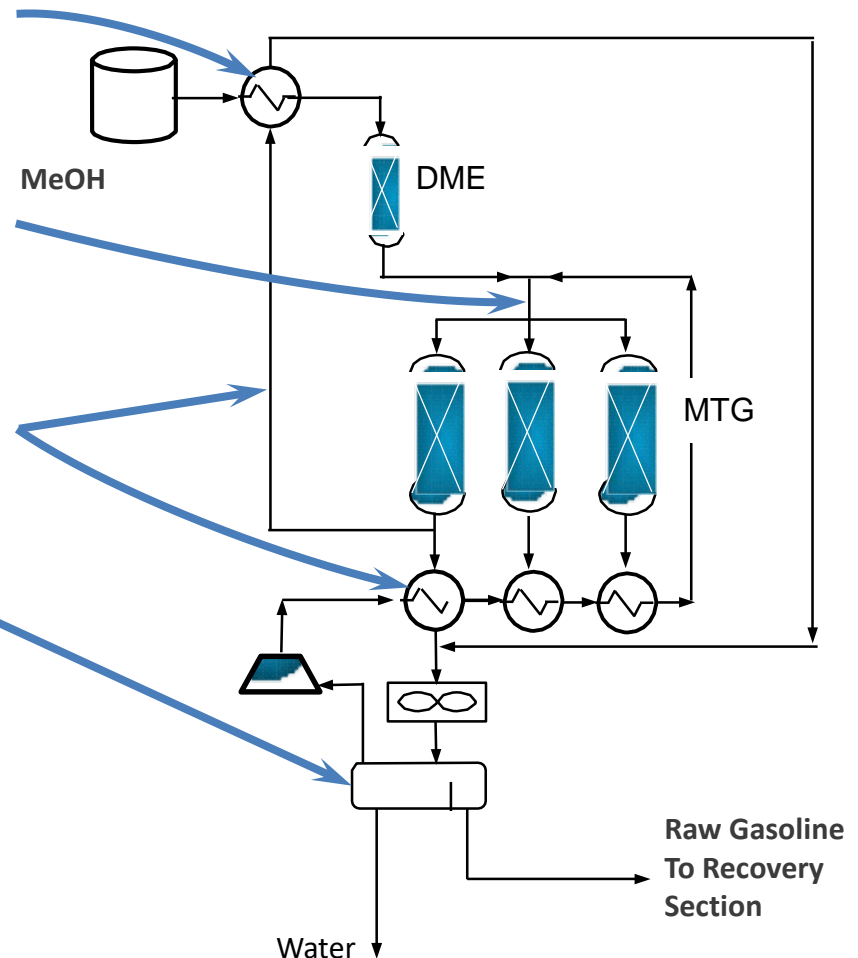
Raw Gasoline Recovery Section
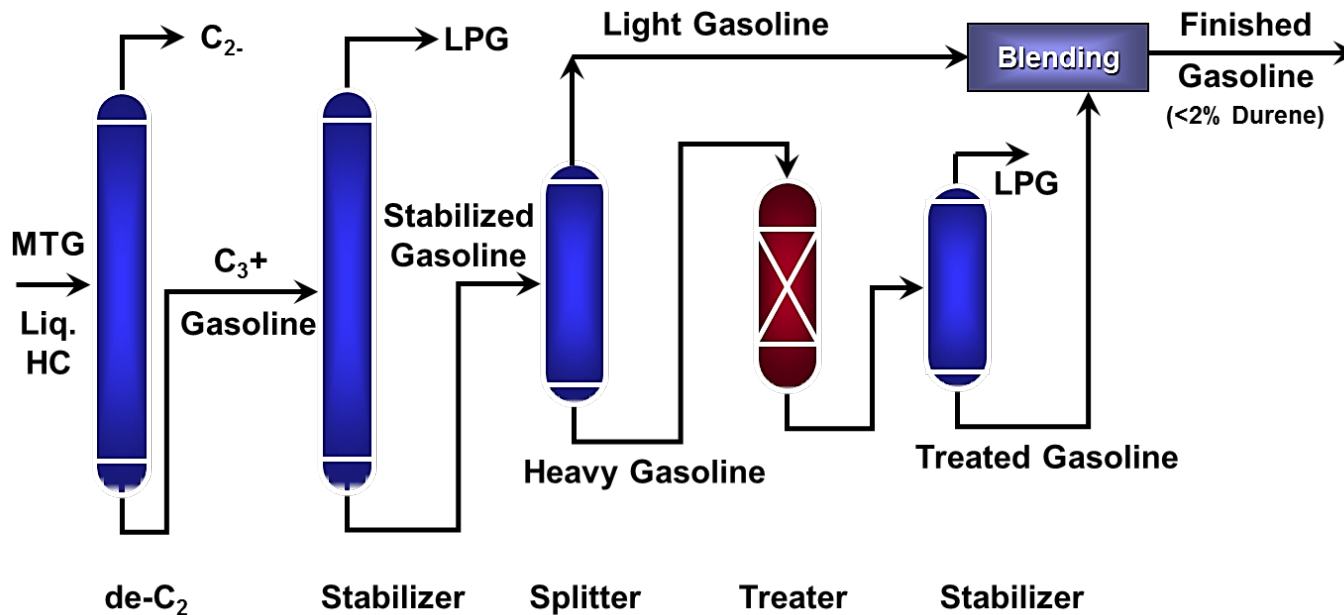
- Raw MTG gasoline is fed to de-ethanizer and stabilizer columns to remove fuel gas and LPG fractions from the gasoline
- Stabilized gasoline is split into light and heavy gasoline fractions
- Heavy gasoline is mildly hydro-treated to reduce Durene (1,2,4,5 tetra-methyl benzene) content (to 2% maximum)
- Treated heavy gasoline and light gasoline are blended into finished product

MTG Reactor System (Multiple)

Methanol

Water

Purge Gas

C2-   LPG

Light Gasoline

Blending

LPG

Gasoline

Heavy Gasoline

Treated Gasoline

Stabilized Gasoline

Stabilizer

DeEthanizer

Splitter

GHT Reactor   Stabilizer

Methanol to Olefins (MTO)

Mobil Technology (Mobil's MTO Process)
Fixed/Fluidized bed reactor,
470-515°C and 3.0-4.5 bar
Catalyst: ZSM-5

UOP Process
Fluidized bed reactor
Catalyst: SAPO-34

Methanol to Olefins (MTO): From Fundamentals to Commercialization. *ACS Catalysis*, **2015**, *5(3)*, 1922-1938.

Stabilizing the framework of SAPO-34 zeolite toward long-term methanol-to-olefins conversion. *Nat Commun* **12**, 4661 (2021). https://doi.org/10.1038/s41467-021-24403-2

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High selectivity and yield to light olefins.

Material	SAPO-34
T atom %	10% Si (gel)
Selectivities (2 hr)	
C_2-C_4 olefins	96
CH_4	1.4
C_2H_6	0.3
C_3H_8	0.9
Stability	
hr at >50% conversion	>40
Coking	
carbon on used catalyst	19% after 54 HOS
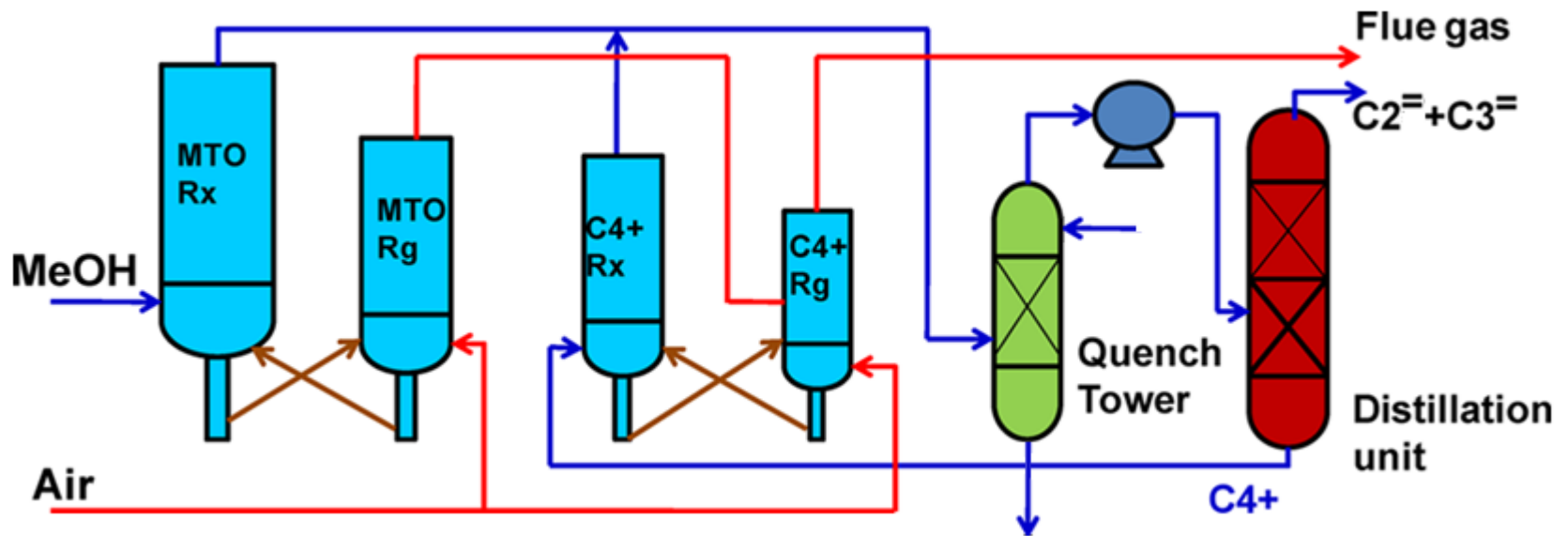
MTO Process Flowsheet
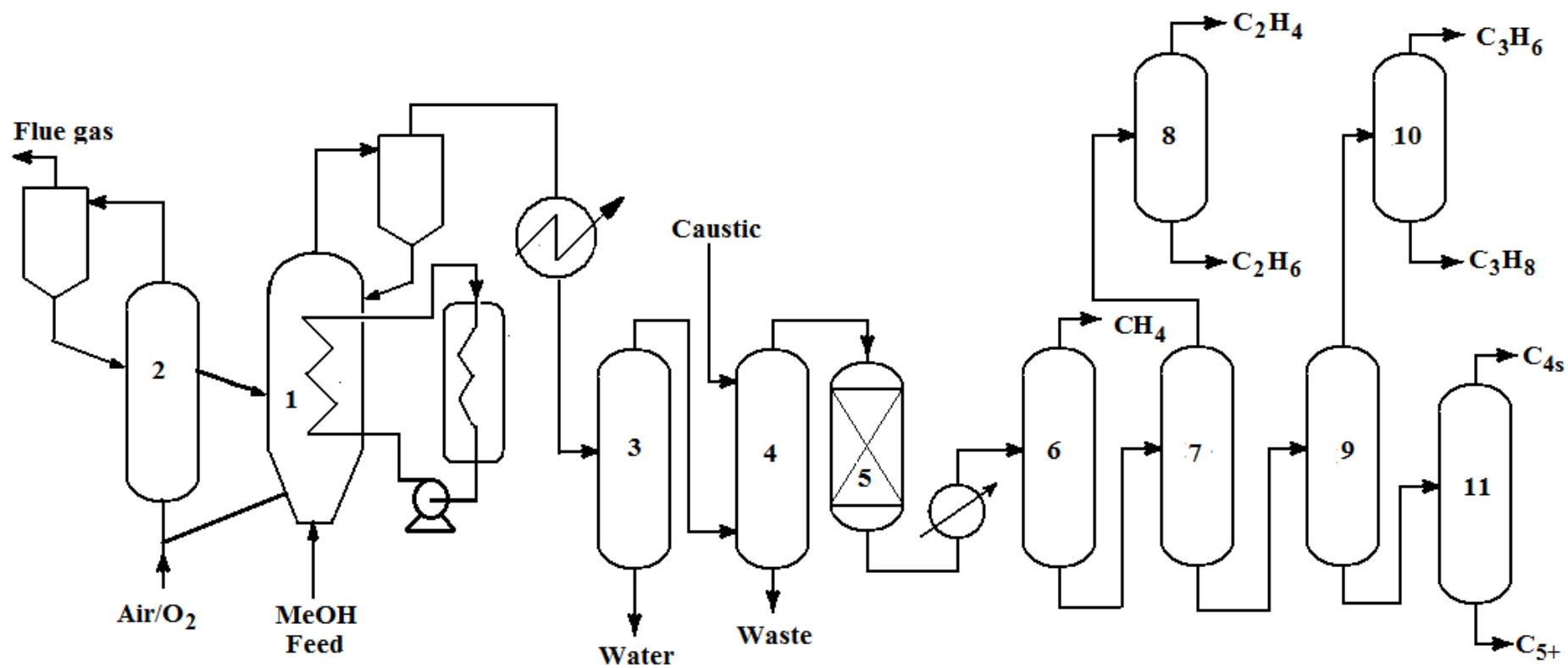
1: Reactor; 2: Regenerator; 3: Separator; 4: Caustic washer; 5: Drier; 6: Demethanizer; 7: Deethanizer; 8: C_2-Splitter; 9: Depropanizer; 10: C_3-Splitter; 11: Debutanizer

Methanol to Propene (MTP)

Lurgi's MTP Process:

Lurgi MTP™ - Methanol-to-Propylene (MTP) is an on-purpose technology for producing propylene from methanol, independently of the original feedstock. The technology offers clients low cash costs, and its propylene product can be used as feedstock for a variety of petrochemical processes.
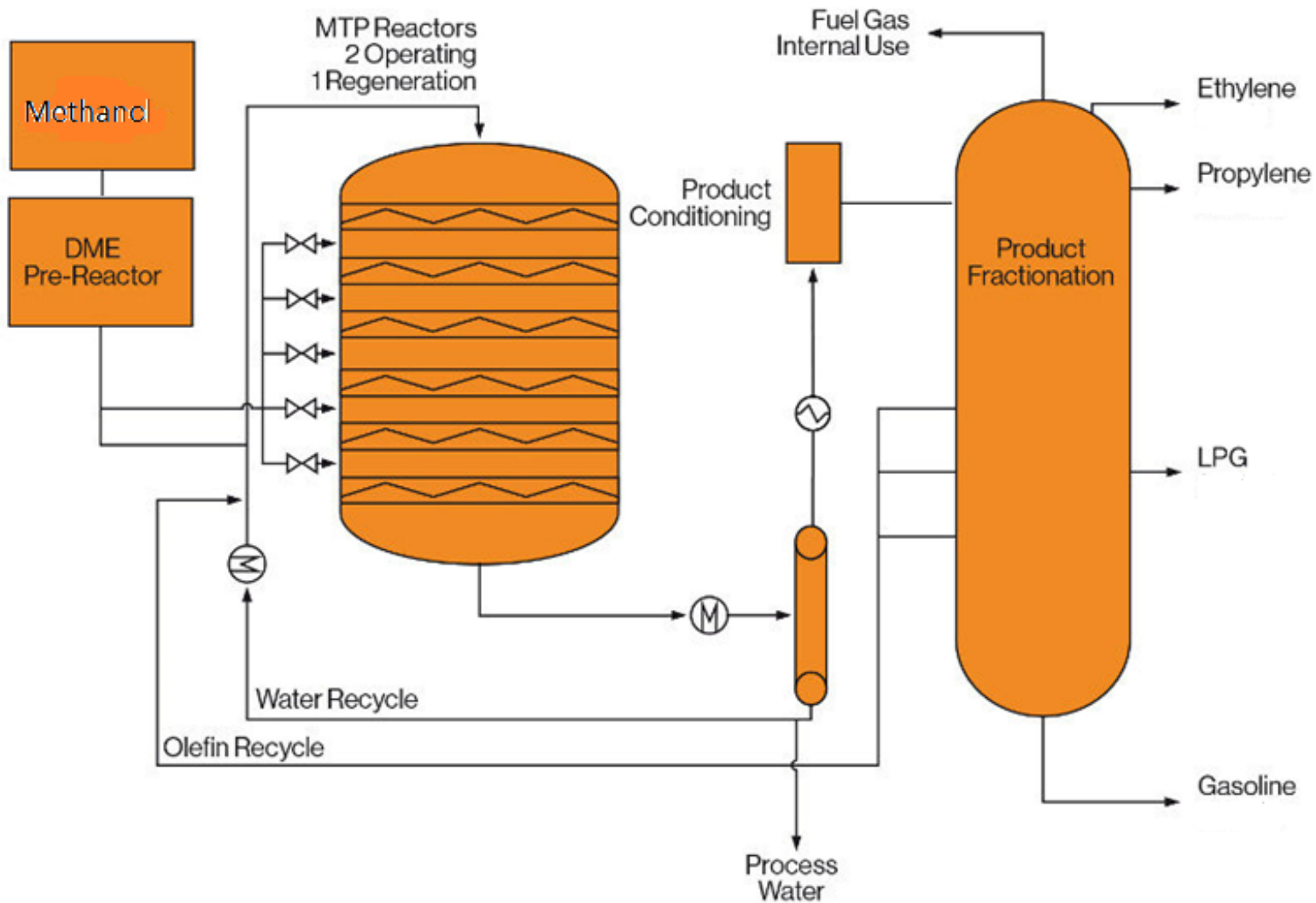
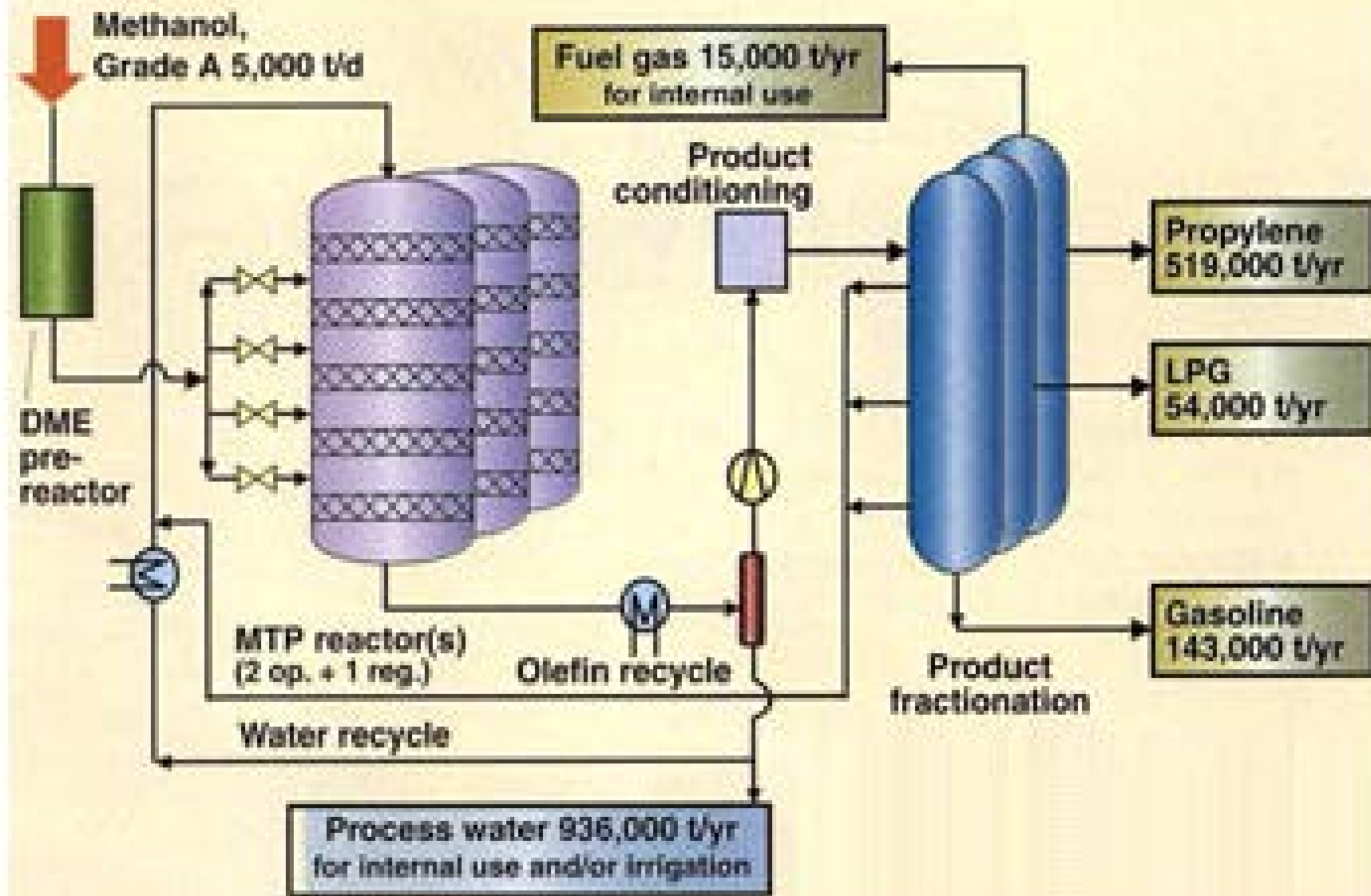ZSM-5 based catalyst developed by Sud-Chemie AG
(Slower deactivation of this catalyst allows the use of a fixed bed reactor technology)

Operates at 425 ^{o}C and 1.5 bar pressure

Propene as the main product
(70% yield and 97% selectivity)

MTP Reactors
2 Operating
1 Regeneration

Methanol

DME
Pre-Reactor

Fuel Gas
Internal Use

Product
Conditioning

Product
Fractionation

Ethylene

Propylene

LPG

Gasoline

Water Recycle

Olefin Recycle

Process
Water

The methanol feed from the Mega-Methanol plant is sent to an adiabatically operated DME (dimethyl ether) pre-reactor where methanol is converted to DME and water using a high-activity high-selectivity catalyst achieving nearly thermodynamic equilibrium. The methanol/water/DME stream is routed to the first MTP reactor where also the steam is added. Methanol/DME are converted to more than 99%, with propylene as the predominant hydrocarbon product. Additional reaction proceeds in the 2nd and 3rd MTP reactors. The process conditions in the three MTP reactors are chosen to guarantee similar reaction conditions and maximum overall propylene yield. The product mixture is then cooled and the product gas, organic liquid and water are separated. The product gas is compressed and traces of water, CO_2 and DME are removed by standard techniques. The cleaned gas is then further processed yielding chemical-grade propylene with a typical purity of more then 97%. Different olefin-containing streams are sent back to the main synthesis loop as an additional propylene source. To avoid accumulation of inert materials in the loop, a small purge is required for light-ends and the C_4/C_5 cut. Gasoline is produced as a by-product. Water is recycled to the steam generation for the process; the excess water resulting from the methanol conversion is purged. Where suitable, this process water can be used for agricultural purposes after appropriate treatment.

The MTP process operates at slightly elevated pressure (1.3-1.6 bara), moderate steam addition (0.5-1.0 kg per kg of methanol) and low reactor inlet temperatures (400-450°C). After a cycle of approx. **400-700 hours** of operation, the catalyst has to be regenerated by burning the coke with a nitrogen/air mixture. The regeneration is carried out at similar temperatures as the reaction itself, hence the catalyst particles do not experience any unusual temperature stress during the in-situ catalyst regeneration procedure. Furthermore, by applying a nitrogen purge after the regeneration is finished, there is no possibility of oxygen breakthrough into the MTP synthesis loop which facilitates reaching the required propylene specification later on in the purification unit. The simplified overall mass balance is depicted in the Figure based on a combined Mega-Methanol/MTP plant. For a feed rate of 5000 t of methanol per day (1.667 million t/a), approx. 519,000 t of propylene are produced per year. By-products include fuel gas and LPG as well as liquid gasoline and process water.

Mobil's Olefin-to-Gasoline and Distillate (MOGD) Process
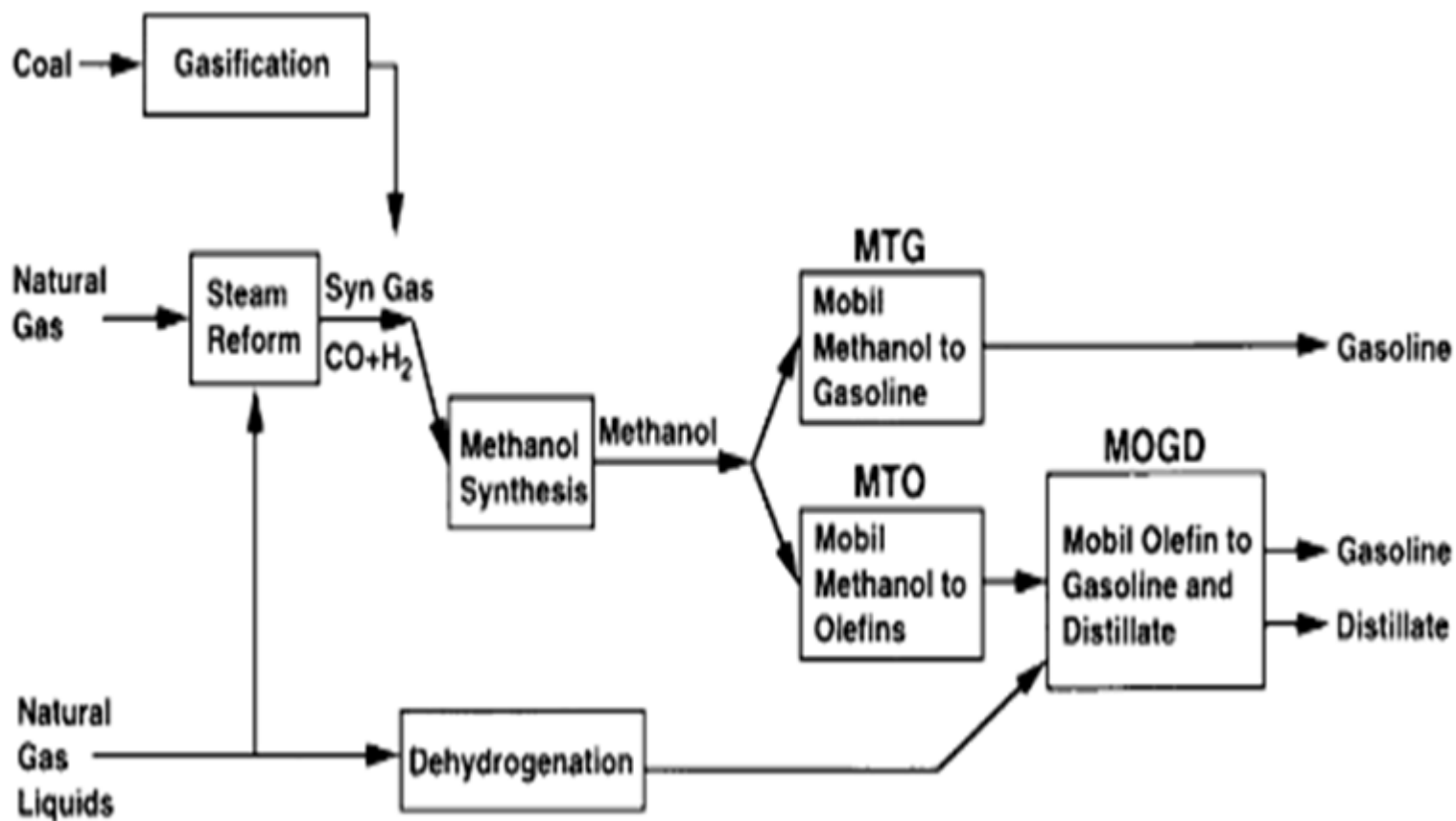
Gasoline and Distillate Production via Methanol and Mobil's ZSM-5 Technology

Both the processes use ZSM-5 as catalyst and the combined MOGD process offers a high valuable gasoline (C5 to C10) and Distillate/diesel (C10 to C20) yield in various proportions – starting from light olefins (C3 to C4).

The gasoline and distillate/diesel selectivity is larger than 95% of the olefins in the feed and the gasoline/distillate product ratios range from 0.2 to >100.

The distillate product is mostly isoparaffinic and is an exceptionally good blending stock due to its high cetane index, low pour point and negligible sulphur content.
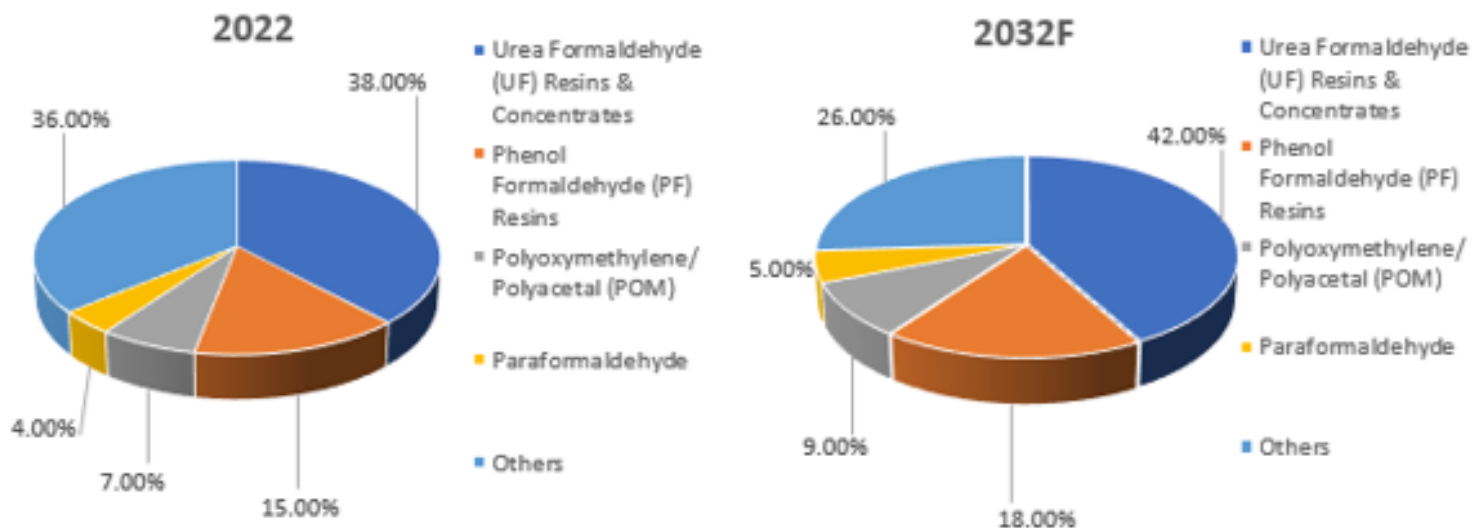
Conditions: 40 to 330 ºC / 0.07 to 140 bar

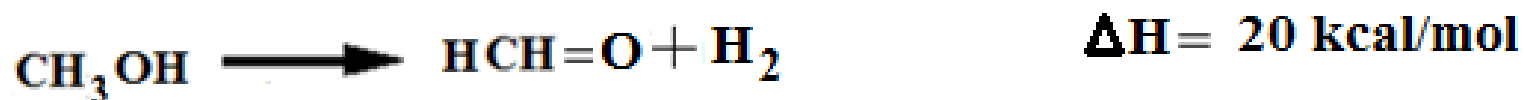**Primary effect of the process variables is to alter the average product molecular weight.**

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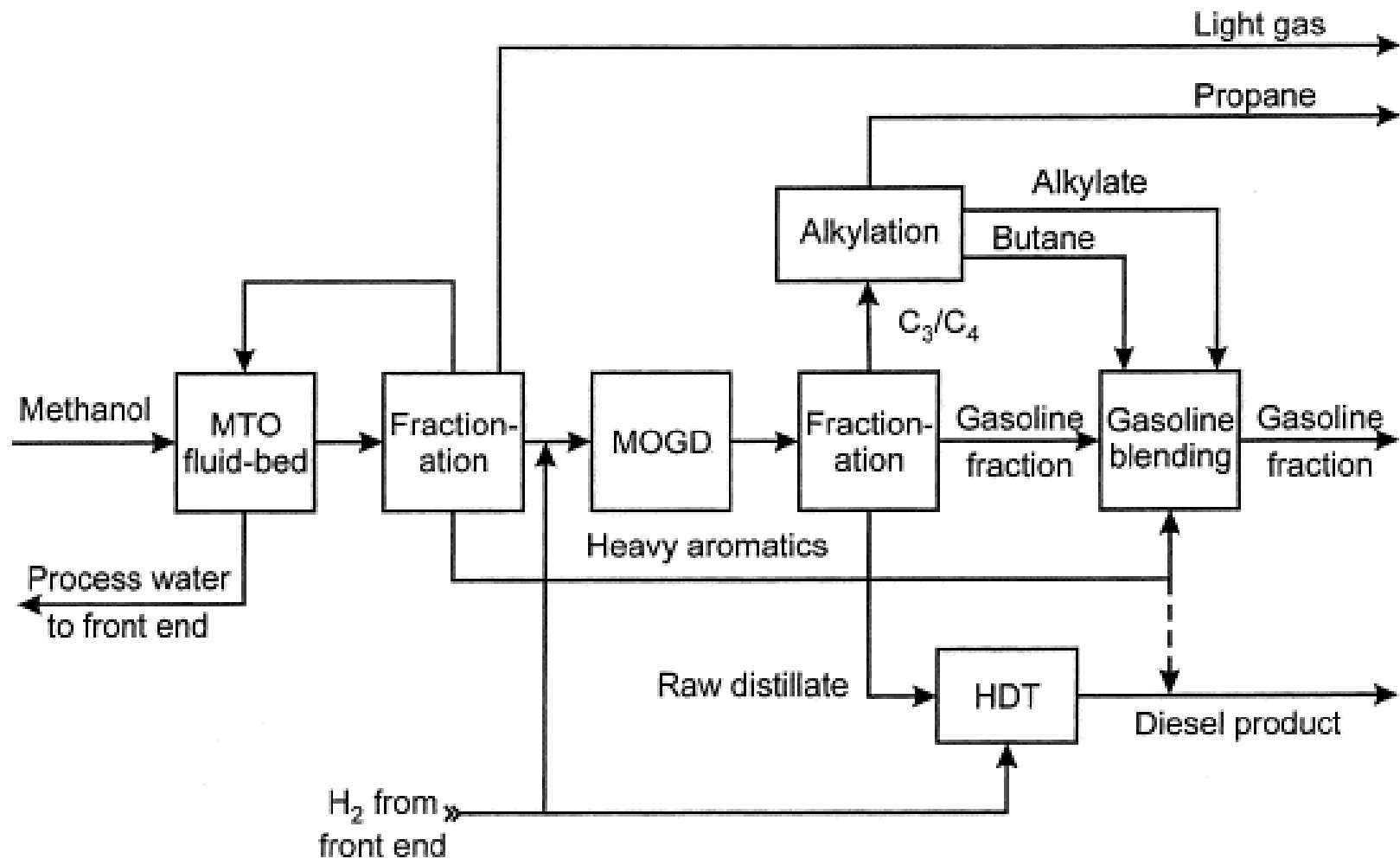
Formaldehyde from Methanol

Formaldehyde is one of the most important chemical products worldwide (production of ~4-5x10^7 tons per year) for the production of urea-phenolic, acetal and melamine resins.

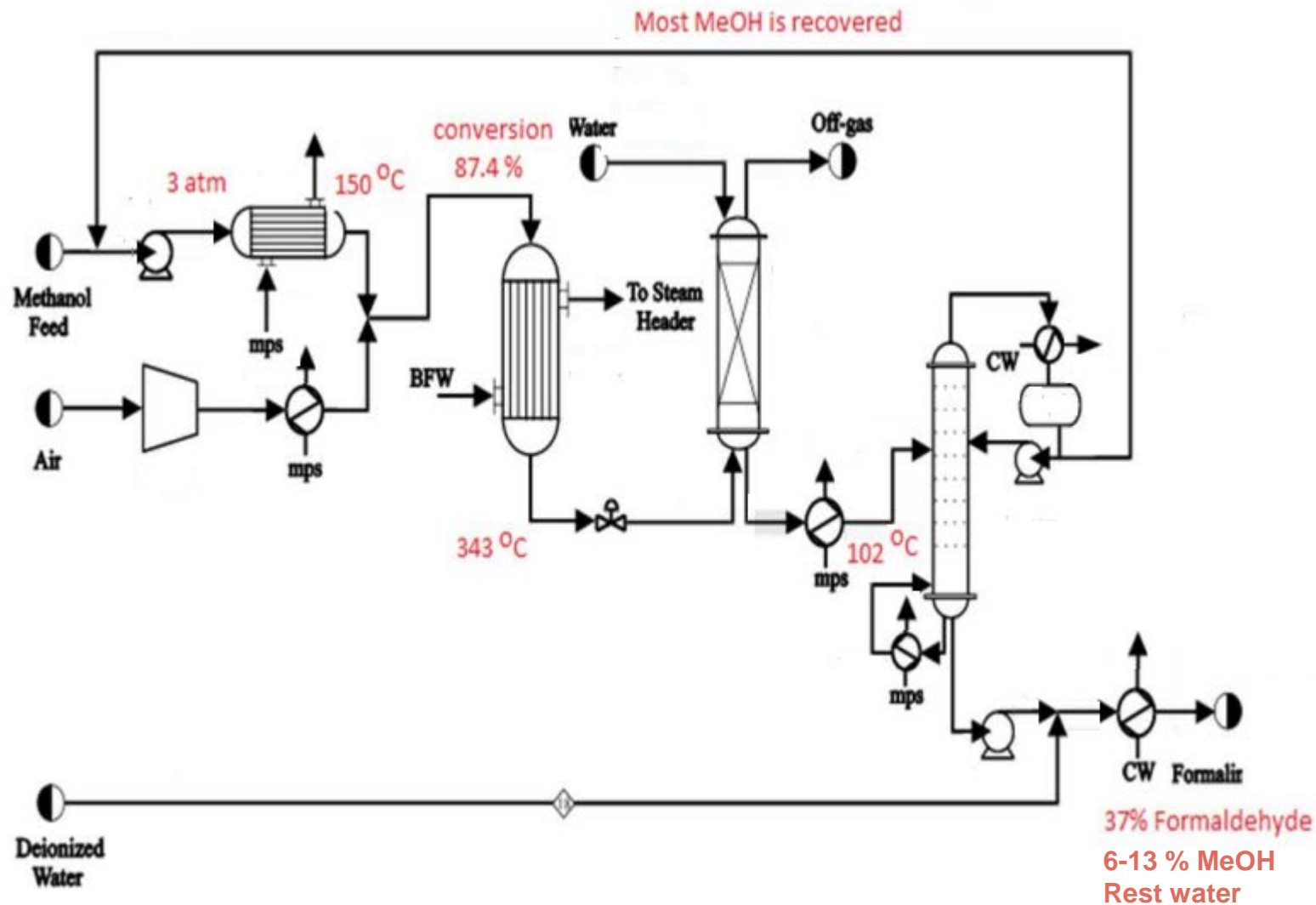Formaldehyde Market Share, By End-Use, By Volume, 2022 & 2032F

Global Formaldehyde Market Size: USD 9.8 Billion

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$$CH_3OH + 1/2\ O_2 \longrightarrow HCH=O + H_2O \quad \Delta H = -38\ kcal/mol$$

$$CH_3OH \longrightarrow HCH=O + H_2 \quad \Delta H = 20\ kcal/mol$$

$$CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2\ H_2O \quad \Delta H = -162\ kcal/mol$$

Catalyst: **Silver gauze or Finely made Copper gauze**

450 – 600 ^{o}C, Atmospheric pressure

MeOH:Air ratio = 0.3 – 0.5

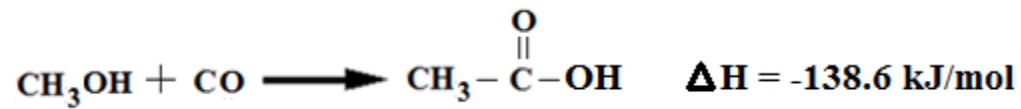Flowsheet for the production of formaldehyde from methanol

Acetic Acid from Methanol

In 2021, market volume of acetic acid worldwide amounted to over 16.7 million metric tons. It is forecast that the market volume of this organic compound will grow to around 22.6 million metric tons worldwide in the year 2029.

Acetic acid is used to prepare vinyl acetate, cellulose acetate, and a miscellany of commercial acetate esters including butyl, ethyl, n-propyl, and iso-propyl. However, the largest volume esters are acetates of glycol ethers. Acetic acid is also used as a solvent in the Amoco process for terephthalic acid.

The preferred industrial method for its manufacture is by the carbonylation of methanol and this accounts for approximately 60 per cent of the total world acetic acid manufacturing capacity.

The carbonylation of methanol, catalyzed by rhodium, was invented by Monsanto in the 1960s and for 25 years was the leading technology.
In 1996 a new, more efficient, process for the carbonylation of methanol was announced by BP Chemicals, using an iridium catalyst.

Ref.: *Platinum Metals Rev.*, **2000**, *44(3)*, 94-105.

$$CH_3OH + CO \longrightarrow CH_3 - \overset{\overset{\displaystyle O}{\parallel}}{C} - OH \qquad \Delta H = -138.6 \text{ kJ/mol}$$

Catalyst: Iodine promoted Rhodium
$200 \,^{\circ}C$, 30-60 atm
99%+ selectivity for acetic acid based on methanol
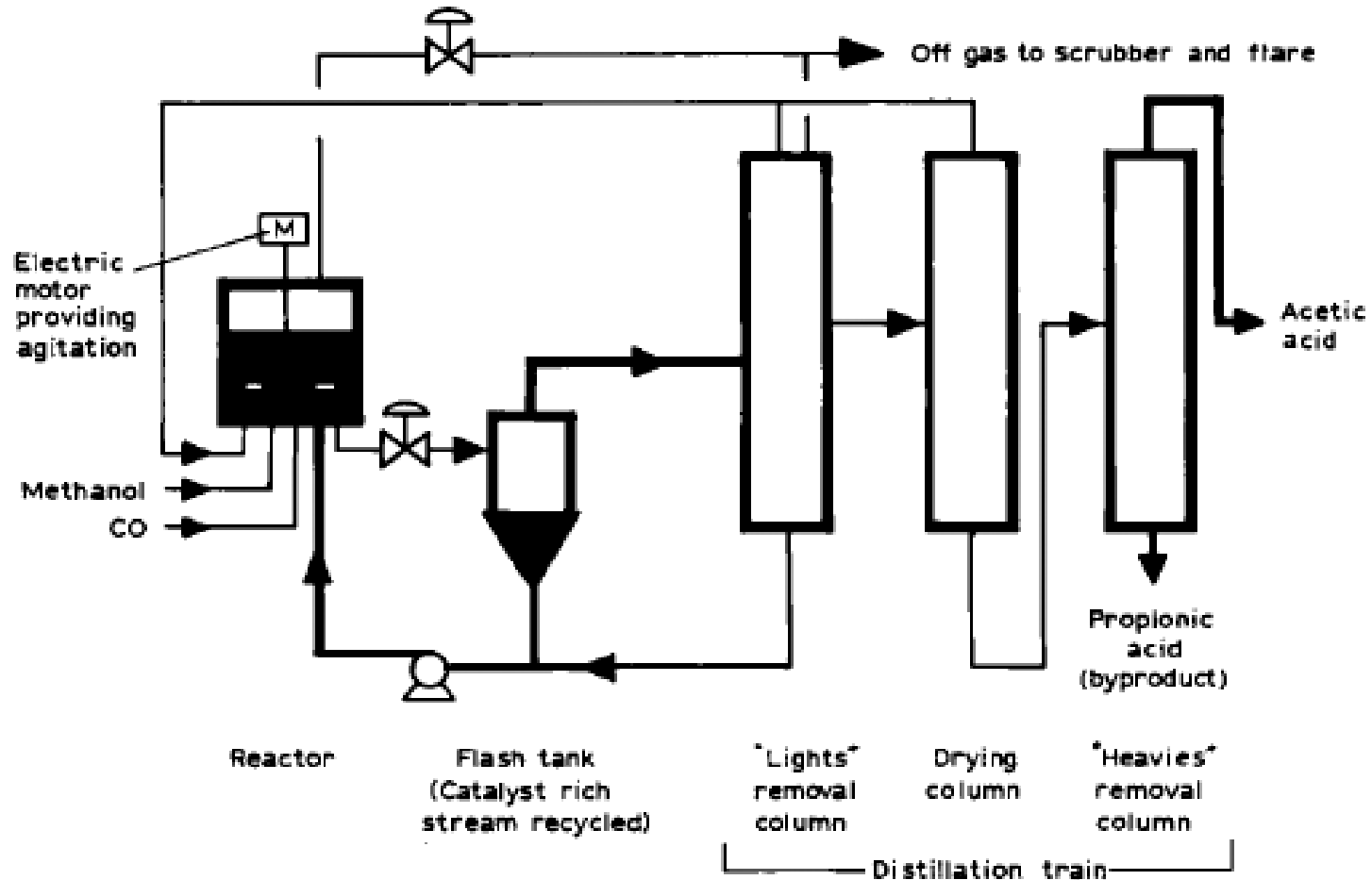
Monsanto Process for Acetic Acid from Methanol
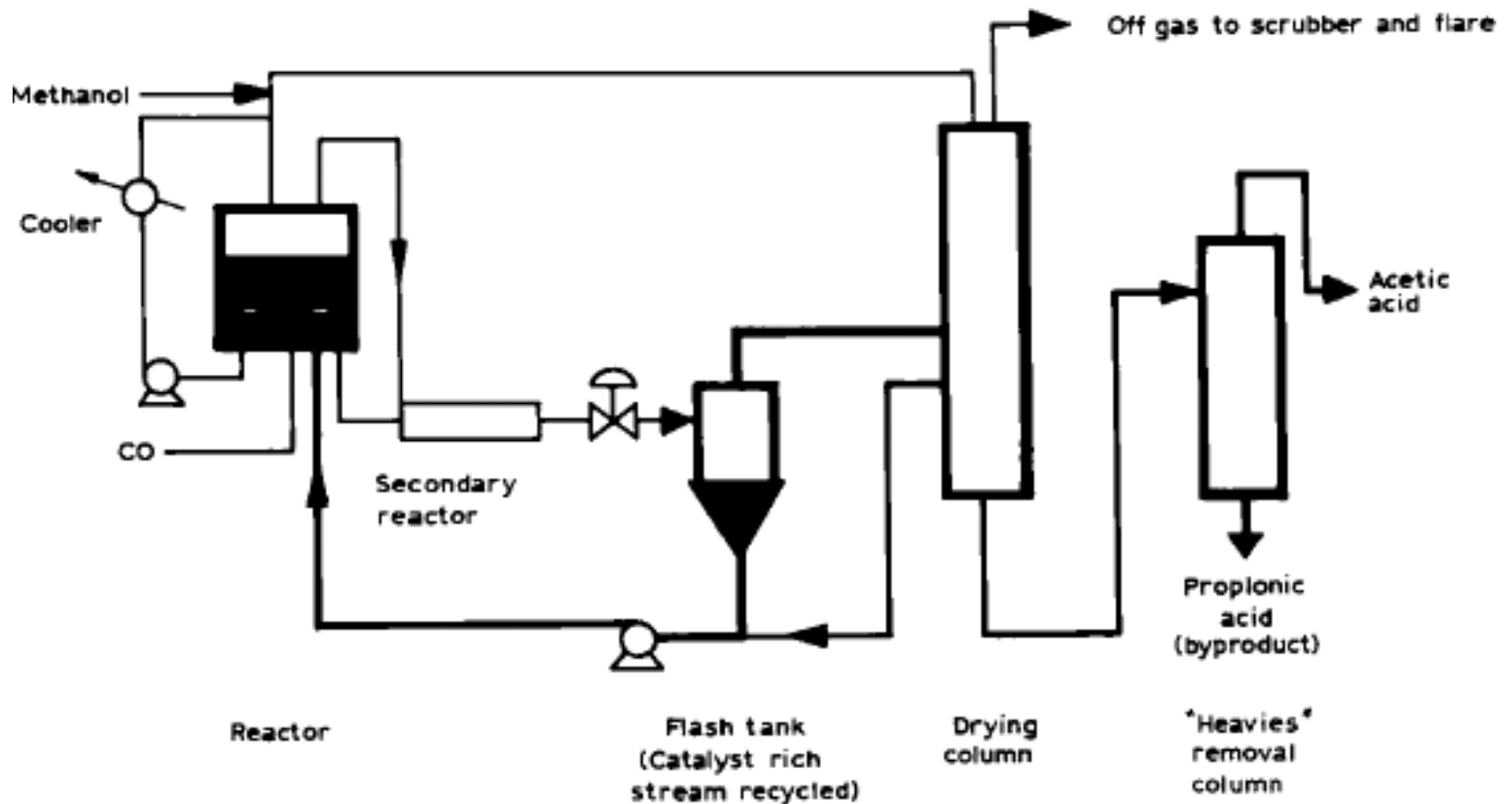
Cativa^{TM} Process

Very similar to the Monsanto Process
Iridium-based catalyst
Advantages are higher stability of the catalyst, less liquid by-products.

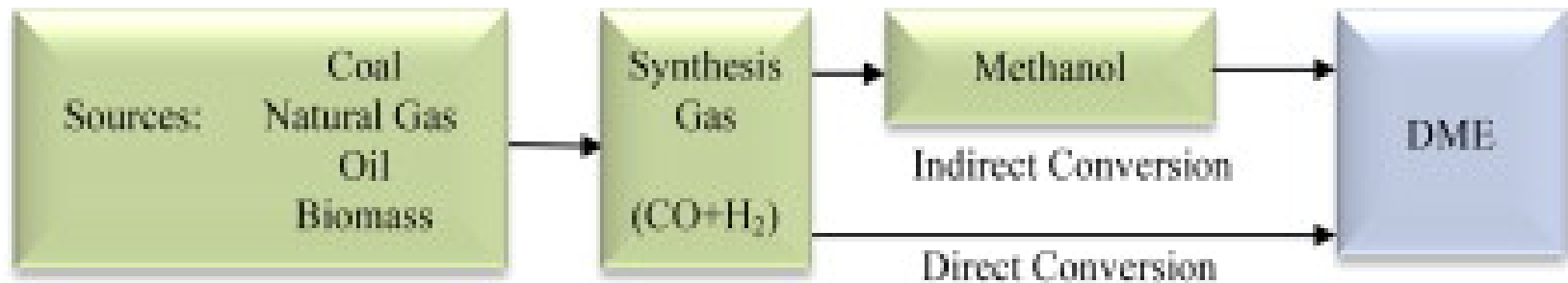Cativa^{TM} Process for Acetic Acid from Methanol

Dimethyl Ether (DME)

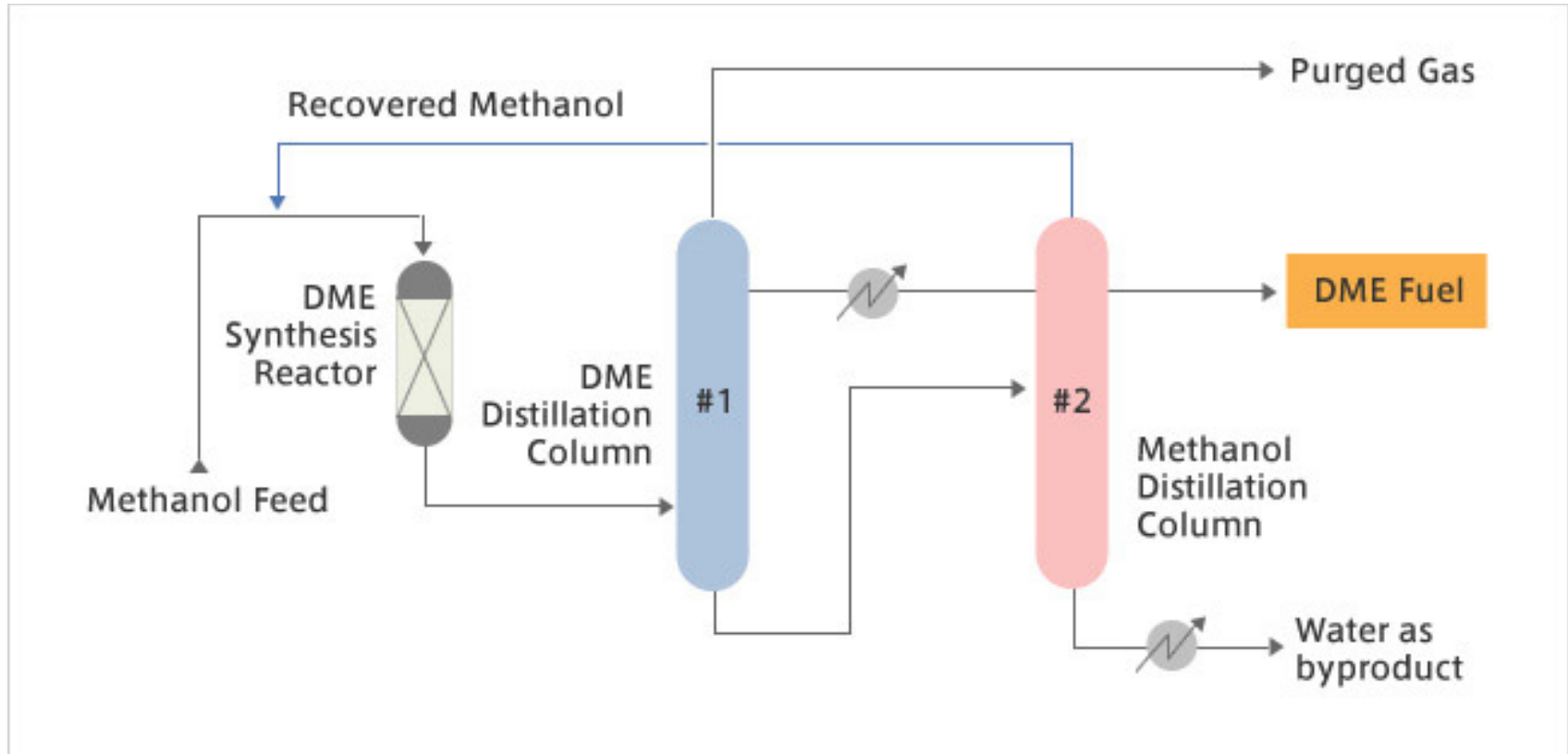DME is used primarily as a propellant.

DME is miscible with most organic solvents and it has a high solubility in water.

The use of DME as a fuel additive for diesel engines has been investigated due to its high volatility (desired for cold starting) and high cetane number.

Sources:
- Coal
- Natural Gas
- Oil
- Biomass

→ Synthesis Gas $(CO+H_2)$

Indirect Conversion → Methanol → DME

Direct Conversion → DME

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H = -23.5\ kJ/mol$$

Production of Dimethyl Ether from Methanol
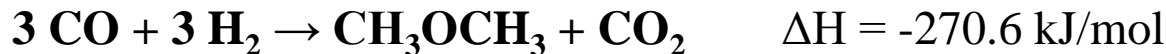
Syngas to DME (STD)

Methanol synthesis from CO:
$$CO + 2 H_2 \rightarrow CH_3OH \qquad \Delta H = -90.4 \text{ kJ/mol}$$

Methanol dehydration:
$$2 CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H = -23.5 \text{ kJ/mol}$$

Water gas shift reaction:
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41.0 \text{ kJ/mol}$$

Methanol synthesis from CO_2:
$$CO_2 + 3 H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H = -44.4 \text{ kJ/mol}$$

Overall reaction:
$$3 CO + 3 H_2 \rightarrow CH_3OCH_3 + CO_2 \qquad \Delta H = -270.6 \text{ kJ/mol}$$

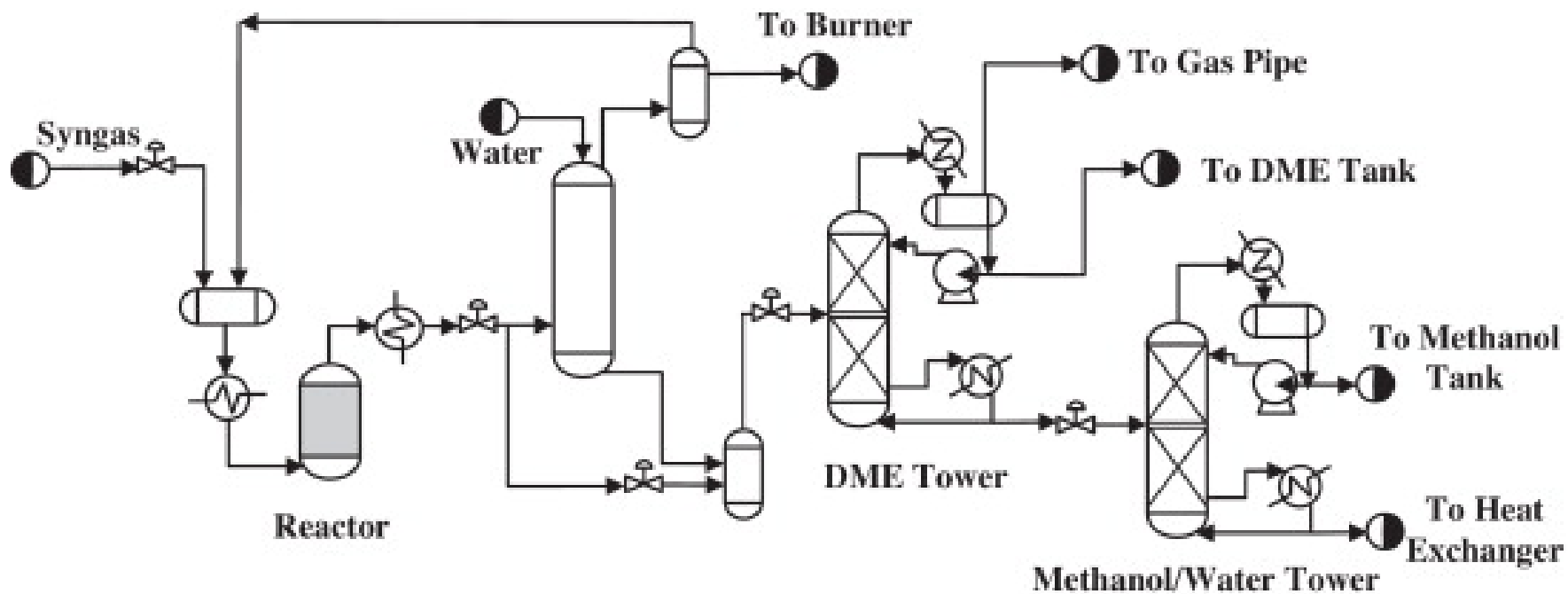**Haldor-Topsoe Process:**

Bifunctional catalyst: Addition of HZSM-5 to the traditional
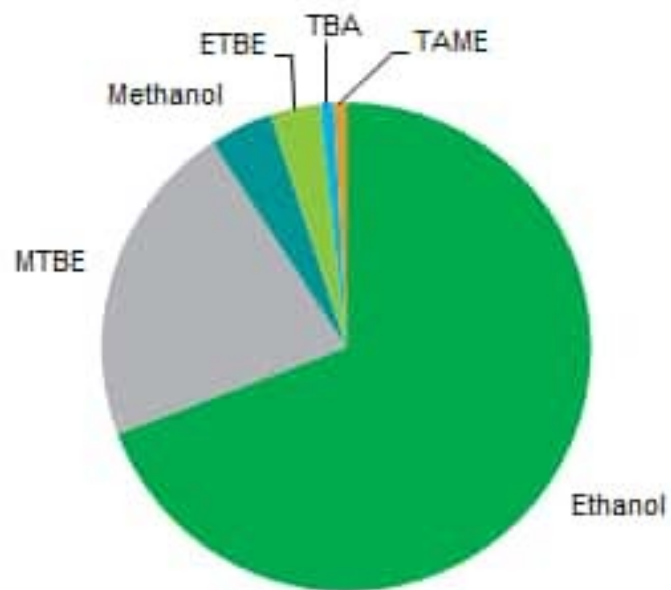$CuO/ZnO/Al_2O_3$ methanol synthesis catalyst
290 – 400 ^{o}C; 80-120 bar

Direct synthesis of DME from syngas (STD)

Thank you

World consumption of gasoline octane improvers/oxygenates—2021

Source: Chemical Market Analytics by OPIS

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	RON	MON
MeOH	129-134	97-104
MTBE/ ETBE/ TAME	105-123	95-105

55

BS IV and BS VI Fuel Standards

Characteristics	Unit	Bharat Stage IV	Bharat Stage VI
Gasoline			
Implementation date		2010 (selected cities), 2017 (nationwide)	2020
Density 15°C	kilograms (kg)/cubic meter (m³)	720–775	720–775
Research octane number (RON)	minimum	91/95[a]	91/95
Anti-knock index (AKI) or motor octane number (MON)	minimum	81/85	81/85
Sulfur, max	ppm	50	10
Lead, max	grams (g)/liter (L)	0.005	0.005
Benzene, max	% volume	1.0	1.0
Aromatics, max	% volume	35	35
Olefin, max	% volume	21/18[a]	21/18[a]
Oxygen content, max	% mass	2.7	2.7
Reid vapor pressure (RVP) @ 37.8ºC, max	kilopascal (kPa)	60	60
Diesel			
Implementation date		2010 (selected cities), 2017 (nationwide)	2020
Ash, max	% mass	0.01	0.01
Carbon residue (Ramsbottom) on 10% residue, max [b]	% mass	0.3	0.3
Cetane number (CN), min	—	51	51
Cetane index (CI), min	—	46	46
Distillation 95% vol. recovery at °C, max	°C	360	370
Flash point Abel, min	°C	35	35
Kinematic viscosity @ 40 °C	centistokes (cSt)	2.0–4.5	2–4.5
Density @ 15 °C	kg/m³	815–845	810–845
Total sulfur, max	milligram (mg)/kg	50	10
Water content, max	mg/kg	200	200
Cold filter plugging point (CFPP) a) summer, max b) winter, max	°C °C	18 6	18 6
Total contaminations, max	mg/kg	24	24
Oxidation stability, max	g/m³	25	25
Polycyclic aromatic hydrocarbon (PAH), max	% mass	8	8
Lubricity, corrected wear scar diameter (wsd 1,4) @ 60 °C, max	μm (microns)	460	460
Copper strip corrosion for 3 hours @ 50 °C	Rating	Class I	Class I

[a] Fuel quality specification for regular/premium gasoline.

[b] This limit is applicable prior to the addition of any ignition improvers. In case a value exceeding the limit is obtained on finished fuels in the market, ASTM D 4046 / ISO 13759 shall be used to establish the presence of nitrate-containing compounds. In such case, the present limit for carbon residue cannot be applied. However, the use of an ignition improver does not exempt the manufacturer from meeting this requirement prior to the addition of additives.

ISO 4264 Petroleum products - Calculation of cetane index of middle-distillate fuels by the four variable equation

5 Procedure

5.1 Determine the density at 15 °C of the sample, to the nearest 0.1 kg/m3, by the procedure described in ISO 3675 or ISO 12185, using the corrections given in ISO 91 if appropriate.

5.2 Determine the temperatures, to the nearest 1 °C, at which 10 % (V/V), 50 % (V/V) and 90 % (V/V) of the sample is recovered during distillation, corrected to standard barometric pressure, by the procedure described in ISO 3405.

5.3 Test method ISO 3924 may be used as an alternative to test method ISO 3405 to determine the 10 %, 50 % and 90 % recovery temperatures of the fuel.

5.4 If test method ISO 3924 is used, convert the ISO 3924 data to estimated ISO 3405 data, following instructions of the former document on the calculation of equivalent data, and use the estimated ISO 3405 data in place of actual ISO 3405 data in the calculations.

6 Calculation

6.1 Calculate the cetane index using the following procedure:
Insert the measured values (see 5.1 and 5.2) in Formula (1) below and calculate the cetane index, CI:

$$CI = 45,2 + 0,089\,2T_{10N} + (0,131 + 0,901B)T_{50N} + (0,0523 - 0,42B)T_{90N} + ...$$

$$... + 0,000\,49\left(T_{10N}^2 - T_{90N}^2\right) + 107B + 60B^2$$

where

$T_{10N} =$ $T_{10} - 215$;

$T_{50N} =$ $T_{50} - 260$;

$T_{90N} =$ $T_{90} - 310$;

T_{10} is the 10 % (*V/V*) distillation recovery temperature, in degrees Celsius;

T_{50} is the 50 % (*V/V*) distillation recovery temperature, in degrees Celsius;

T_{90} is the 90 % (*V/V*) distillation recovery temperature, in degrees Celsius;

$B =$ $[\exp(-0,003\,5D_N)] - 1$;

$D_N =$ $D - 850$;

D is the density at 15 °C, in kilograms per cubic metre.