Hydrocarbon Processing

Gasoline component technologies

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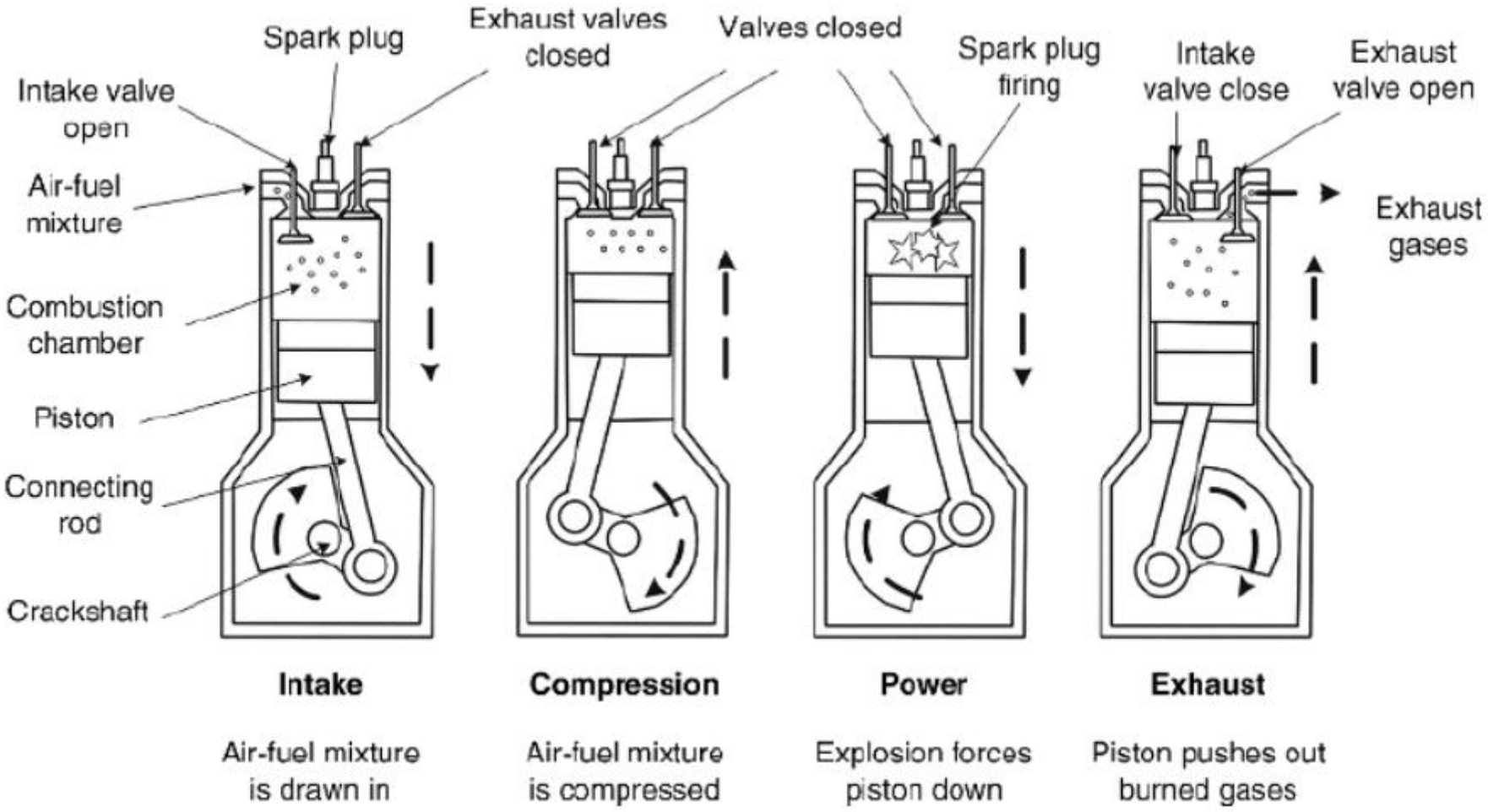
BME
2023

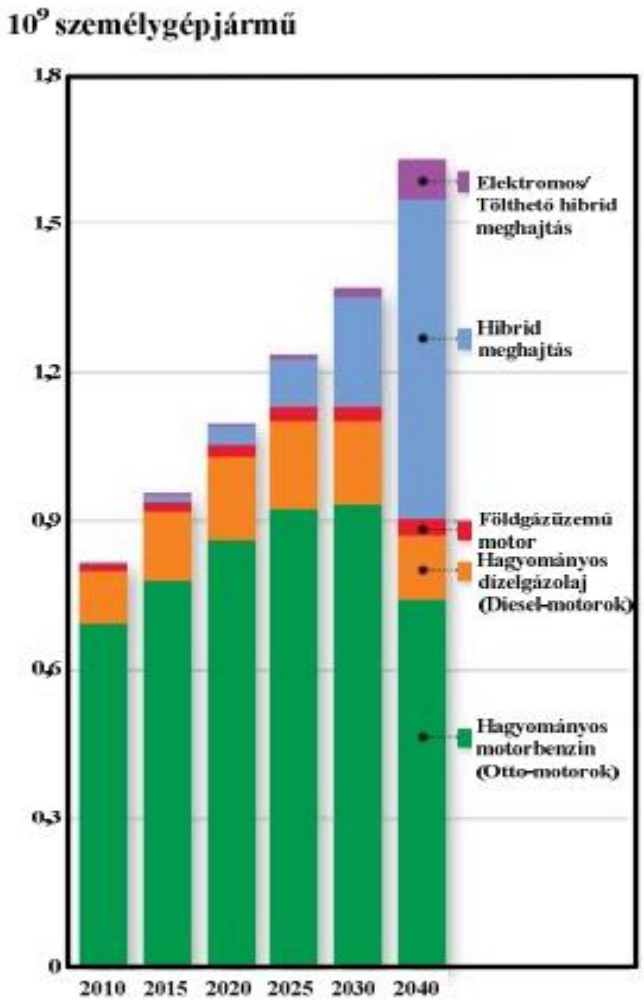
Otto-engine operation

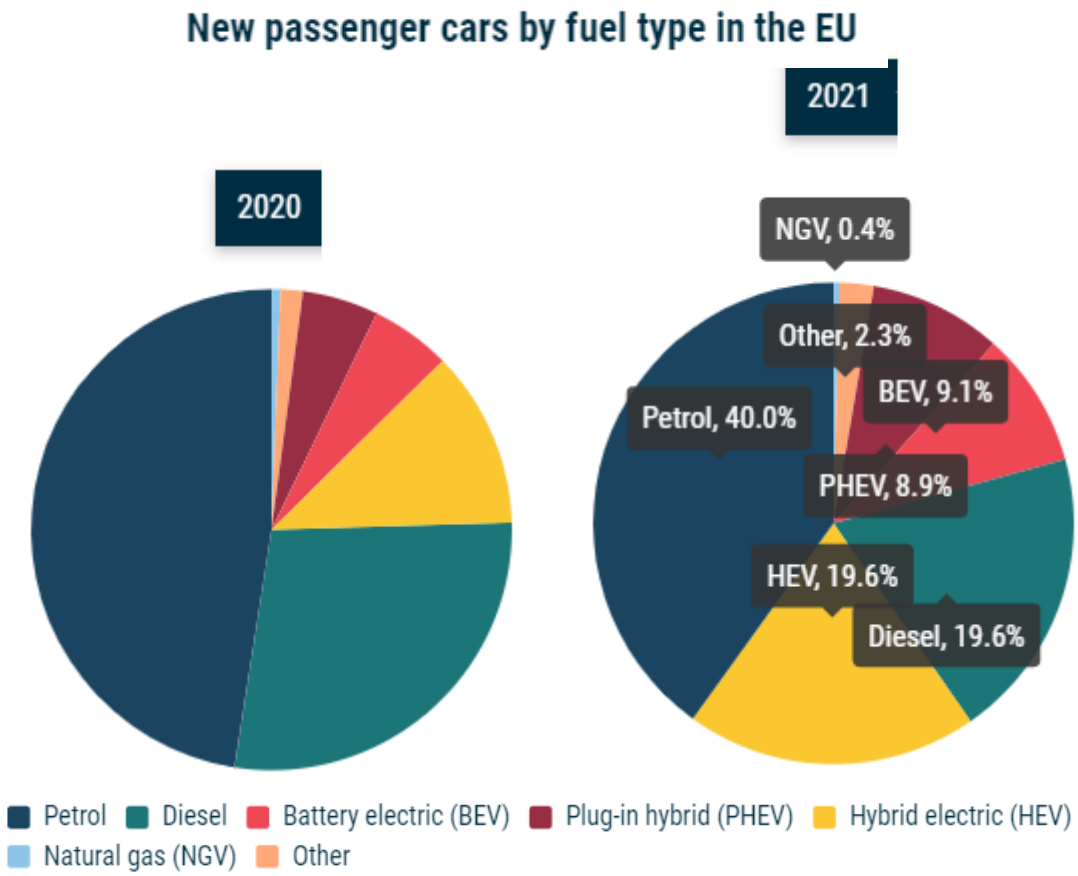


Prices on 2023.10.18.

- Mineral water: 80-200 Ft/l
- Milk: 300-700 Ft/l
- Coke: 300-500 Ft/l
- Beer: 500-1500 Ft/l
- Brent crude: 90,28 $/bbl
- USD/HUF: 363,47
- Crude price: 91,41/159*363,47=208,96 Ft/l
- Gasoline: 605 Ft/l

Passenger car distribution by **drive/fuel type**





Exxon Mobil: “The Outlook for Energy: A View to 2040”, 2014
https://www.acea.auto/fuel-pc/fuel-types-of-new-cars-battery-electric-9-1-hybrid-19-6-and-petrol-40-0-market-share-full-year-2021/

Gasoline standard (MSZ EN 228)

	Jellemző	Mérték-egység	Vizsgálati módszer	Követelmény	
				Esz-95	Esz-98
♣	Kísérleti oktánszám	-	MSZ EN ISO 5164	≥ 95.0	≥ 98.0
	Motoroktánszám	-	MSZ EN ISO 5163	≥ 85.0	≥ 88.0
♣	Etanoltartalom	v/v%	MSZ EN ISO 22854	≤ 10	
	Ólomtartalom	mg/l	MSZ EN 237	≤ 5	
♣	Sűrűség 15 °C-on	g/cm^3	MSZ EN ISO 12185	0.720 - 0.775	
♣	Kéntartalom	mg/kg	MSZ EN ISO 20846	≤ 10	
	Gyantatartalom, oldószerrel mosott	mg/100ml	MSZ EN ISO 6246	≤ 5	
	Korróziós fokozat, 3ó, 50°C	-	MSZ EN ISO 2160	1. osztály	
♣	Benzol	%(V/V)	MSZ EN 12177	≤ 1.0	
	Oxigéntartalom	%(m/m)	MSZ EN ISO 22854	≤ 3,7	
♣	Aromástartalom	%(V/V)	MSZ EN ISO 22854	≤ 35.0	
	Olefintartalom	%(V/V)	MSZ EN ISO 22854	≤ 18.00	
	Külső megjelenés	-	Érzékszervi	tiszta és átlátszó	

Gasoline standard (MSZ EN 228)

Illékonysági osztályok

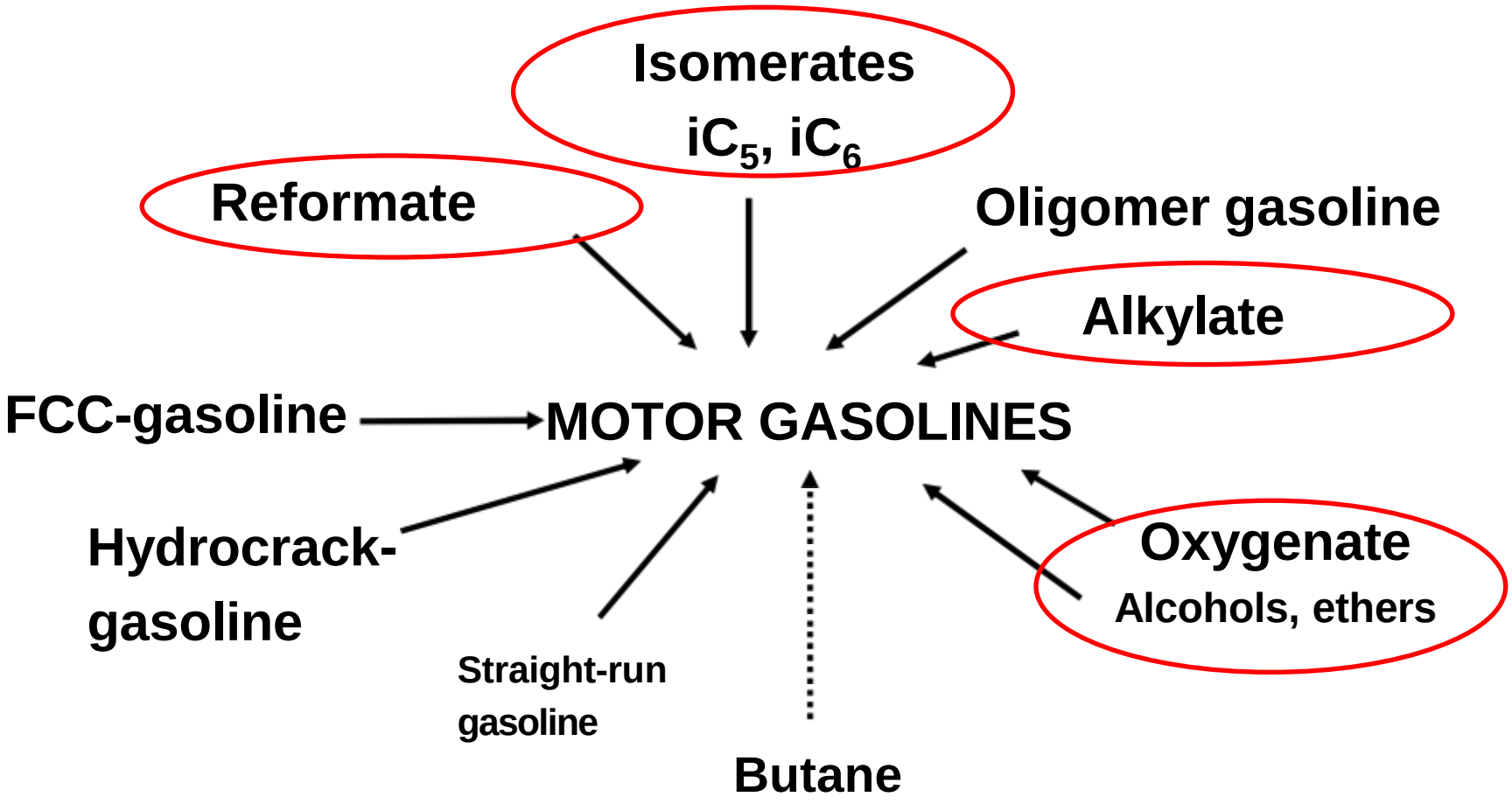
			Nyáron	Télen	Átállási időszakban
Gőznyomás DVPE	kPa	MSZ EN 13016-1	45 - 60	50 - 80 vagy 60 - 90	50 - 80 vagy 60 - 90
70 °C-ig átdesztillált mennyiség	%(V/V)	MSZ EN ISO 3405	20 - 48	22 - 50	22 - 50
100 °C-ig átdesztillált mennyiség	%(V/V)	MSZ EN ISO 3405	46 - 71	46 - 71	46 - 71
150 °C-ig átdesztillált mennyiség	%(V/V)	MSZ EN ISO 3405	≥ 75	≥ 75	≥ 75
♣ Végforrpont °C	°C	MSZ EN ISO 3405	≤ 210	≤ 210	≤ 210
Lepárlási maradék	%(V/V)	MSZ EN ISO 3405	≤ 2	≤ 2	≤ 2

MOTOR GASOLINE

Blending components **Additives**

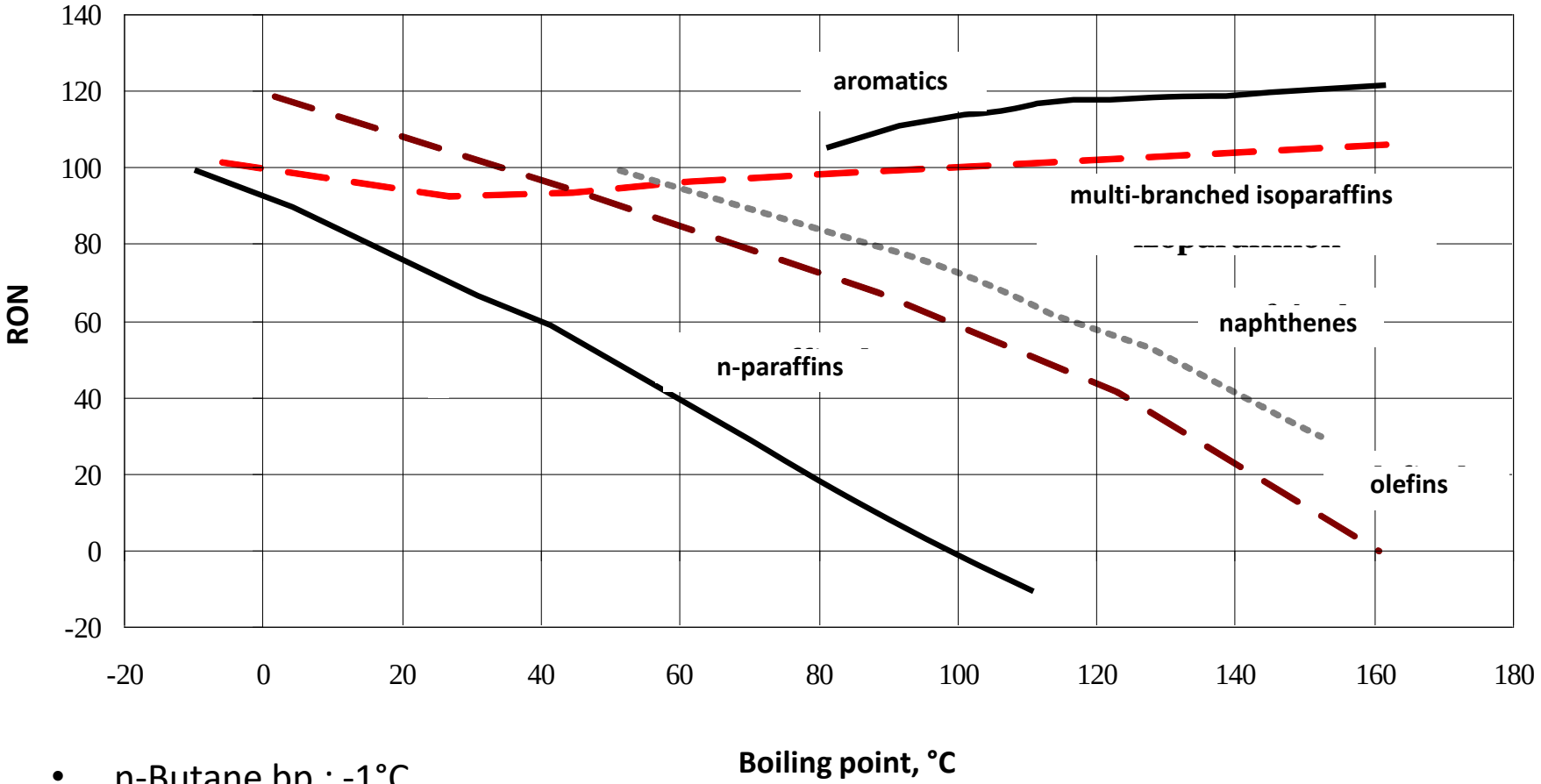
Additives are covered later in the „Blending” lecture.
They are used in small quantities and tehere are several type of them. They improve the quality or the performance of the gasoline.

Motor gasoline **blending components**



1. Light Naphtha Isomerisation

Goal of isomerisation: octane number improvement



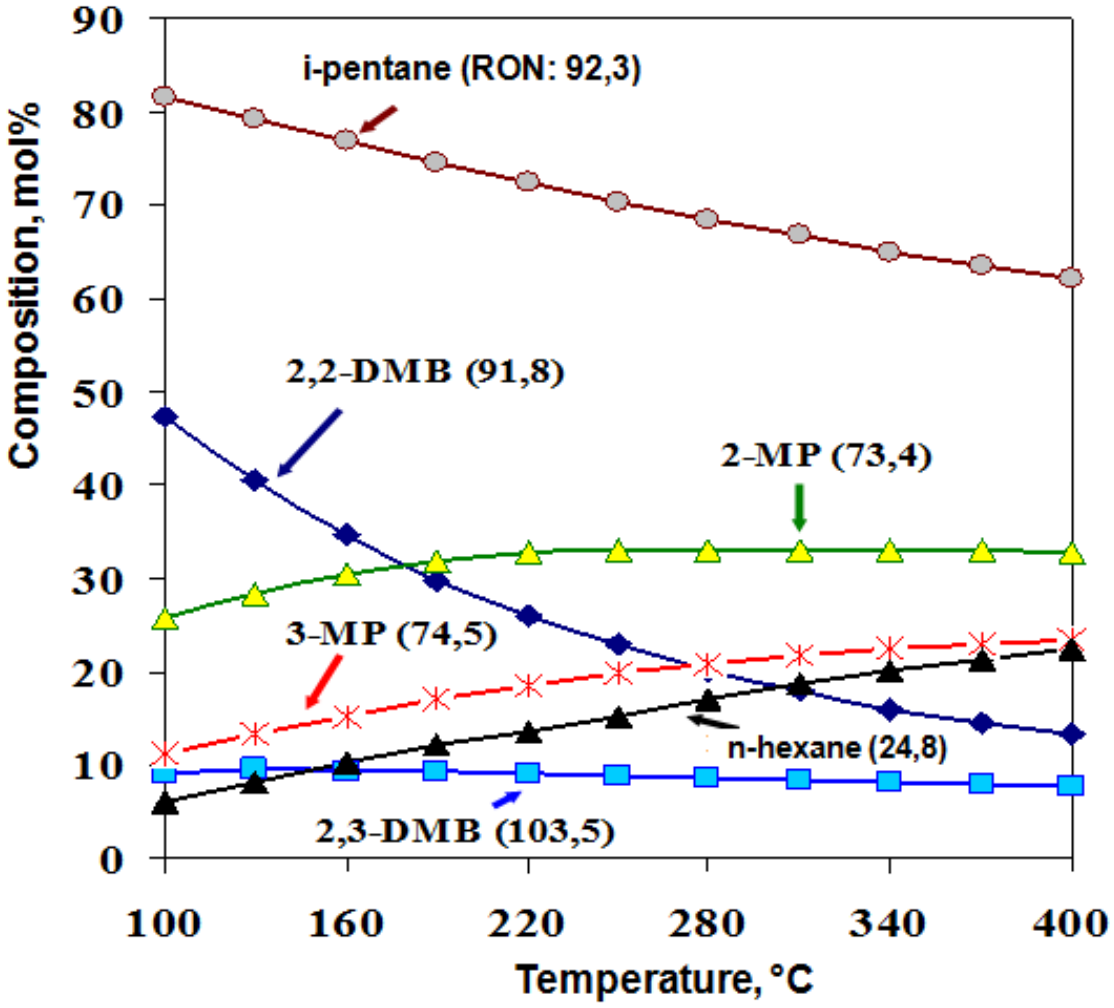
- n-Butane bp.: -1°C
- n-Pentane bp.: 36 °C
- n-Hexane bp.: 69 °C
- n-Heptane bp.: 98 °C – RON=0 reference molecule
- 2,2,4-trimethyl-pentane bp: 99 °C – RON=100 reference molecule

Thermodynamics of isomerisation

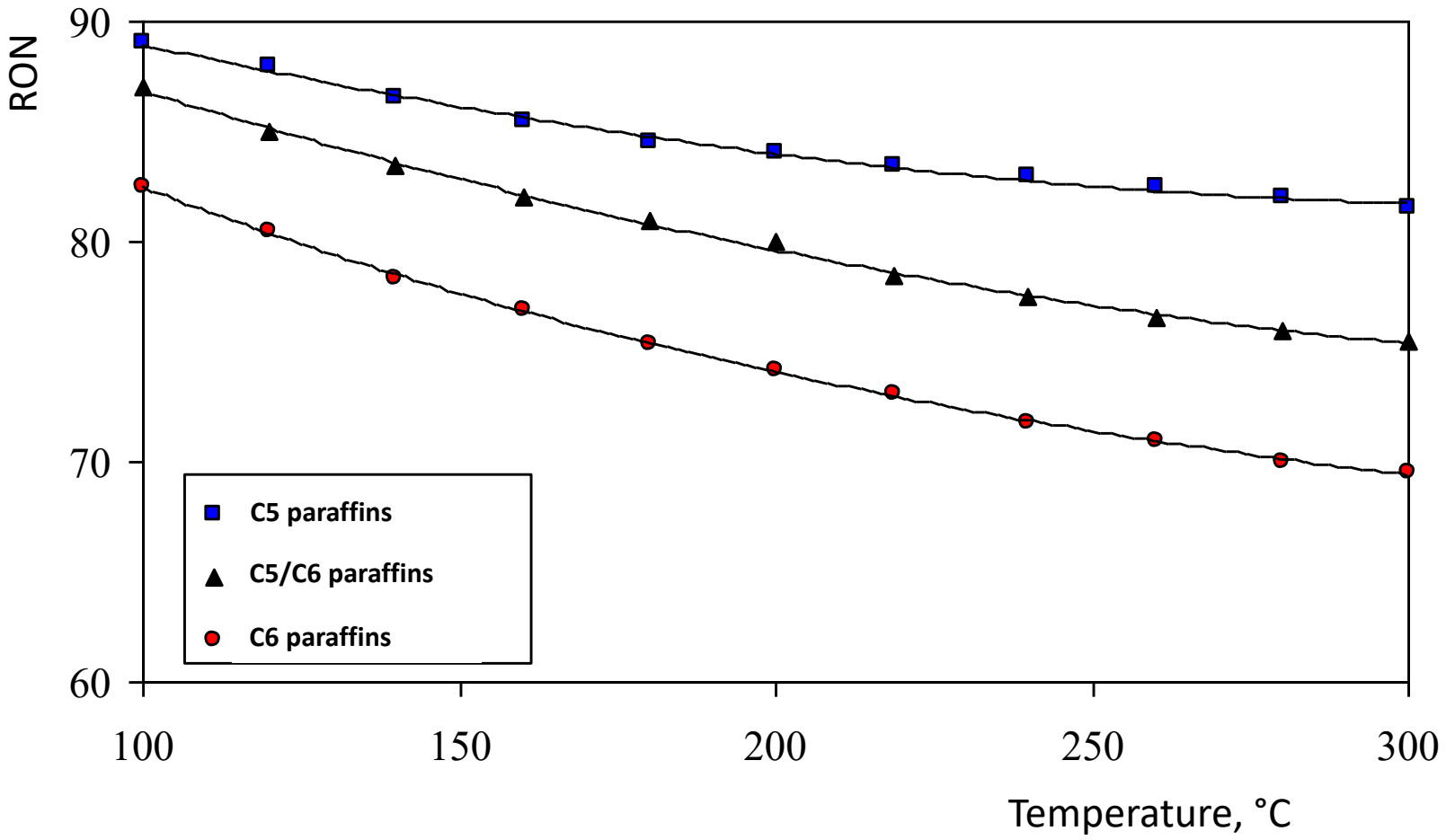
Paraffin hydrocarbon	Reaction heat (25°C), kJ/mol
from n-pentane	
2,2-dimethyl-propane	-19,93
2-methyl-butane	-8,04
from n-hexane	
2,2-dimethyl-butane	-18,39
2,3-dimethyl-butane	-10,59
2-methyl-pentane	-7,12
3-methyl-pentane	-4,44

- Gross **lightly exotherm** process

Equilibrium concentration of pentane and hexane isomers



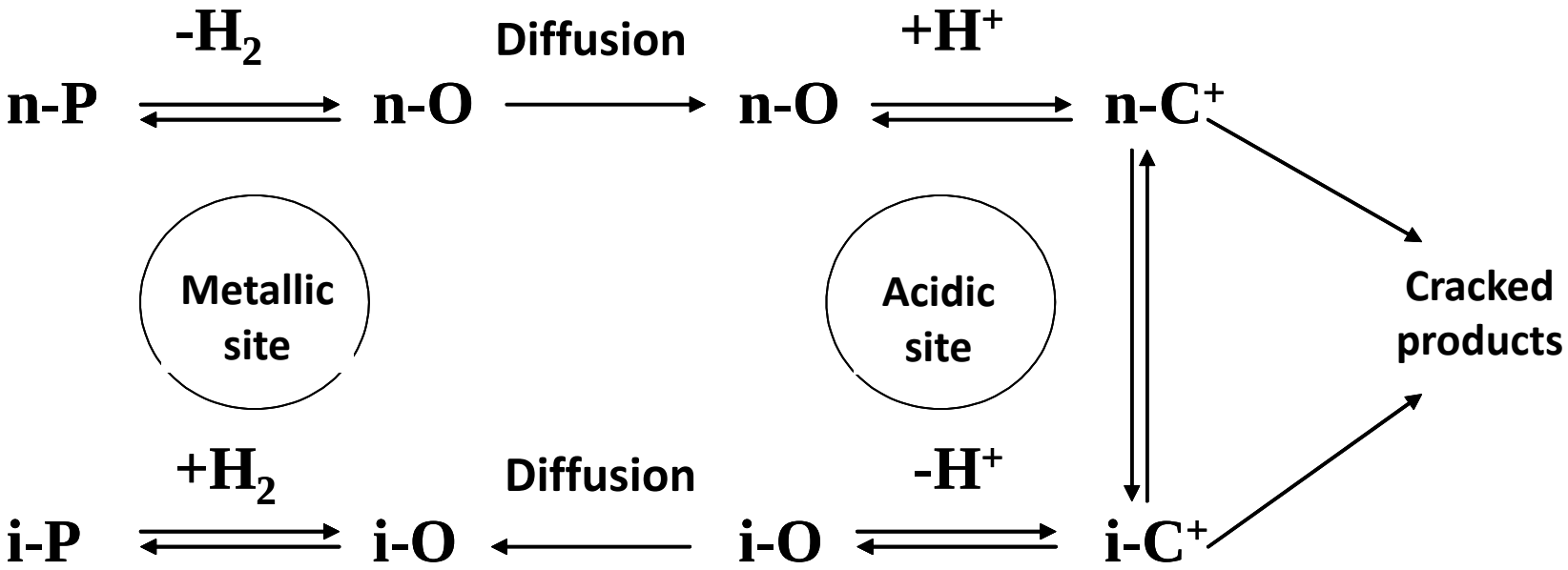
RON of C5-C6 hydrocarbons equilibrium mixtures (open chained)



Hydroisomerisation catalysts

Temperature of favourable activity:

High	Medium	Low
≥300°C	**200°C-300°C**	**≤200°C**
Pt(0,5-0,6)/g-Al_2O_3/F F: 3-4%	Pt(0,3-0,5)/H-Y zeolite Pt(0,3-0,5)/H-Mordenite	Pt(0,3-0,4%)/Al_2O_3/chloride (7-10%) Pt/sulphated metal-oxide Mixed metal-oxide



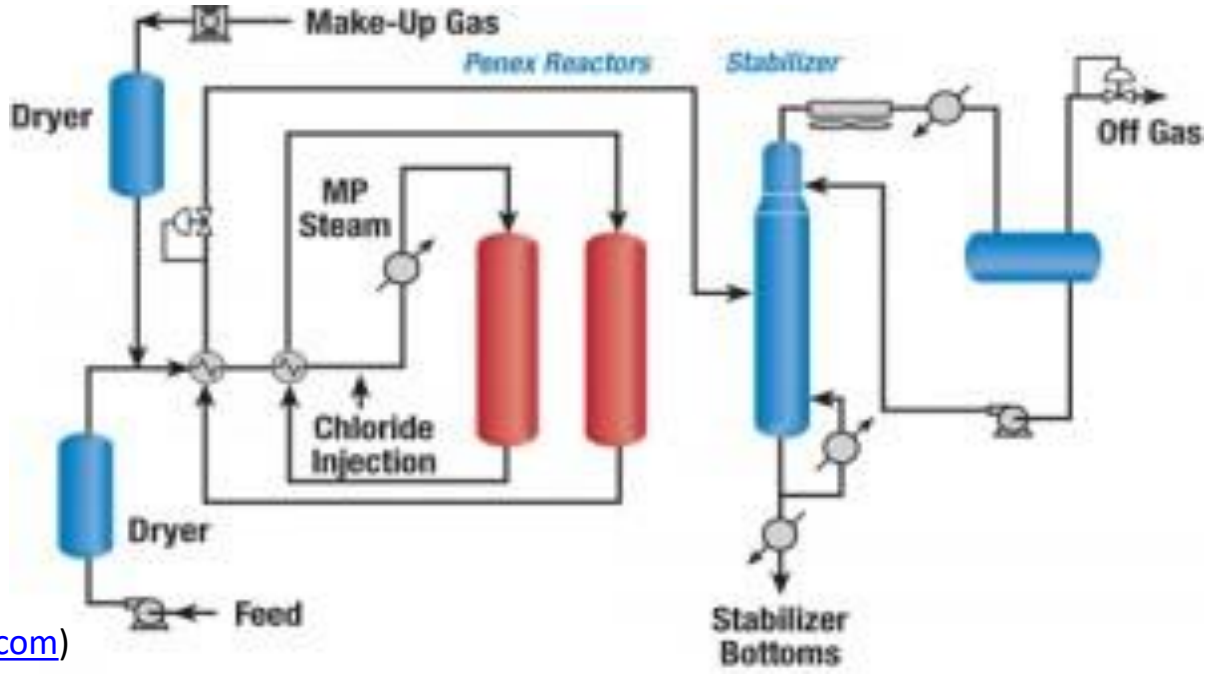
Mechanism of isomerisation on bifunctional catalyst

Advantages of low temperature isomerisation

- Feed and energy efficiency
- Higher isoparaffin yield
- Higher RON
- Lower hydrogen consumption

LN isomersation

- **Aim:** nC_{5-6} transformation to iC_{5-6}
- **Feedstock:** light naphtha
- **Process parameters:** 150-250°C, 20-30 bar
- **Heat balance:** exothermic
- **Catalyst:** Pt/Al_2O_3
- **Products:** iC_5, iC_6



Source: UOP (www.uop.com)

2. Catalytic reforming

Goal of reforming

- **Goal:**
  - Production of high octane gasoline blending components
  - Production of hydrocarbon mixture suitable for individual aromatics recovery
- **Feed:**
  - Desulphurised heavy gasoline (<1 ppm S)
- **Reactions:**
  - Several, complex route

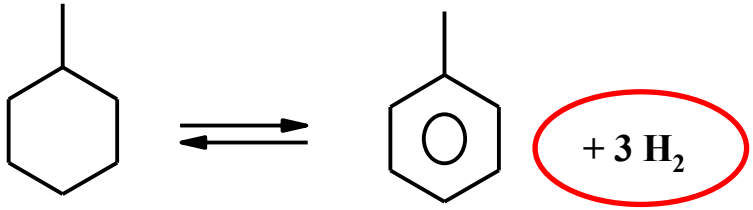
Main reactions 1.

Dehydrogenation

cycloparaffin → aromatic

Reaction heat

$\Delta H = +205$ kJ/mol



Specific gravity, g/cm3	0,7694	0,8669
RON:	73,8	119,7

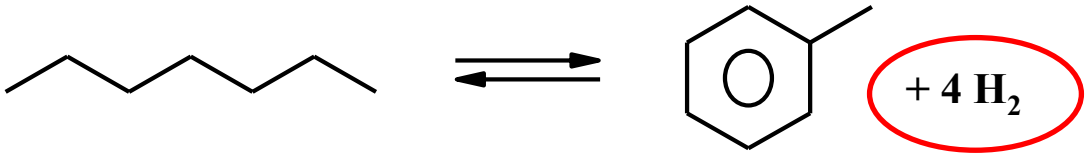
paraffin → olefin

$\Delta H = +90$ kJ/mol

Specific gravity, g/cm3	0,6838	0,7026
RON:	0	89,8

Dehydrocyclisation

$\Delta H = +238$ kJ/mol



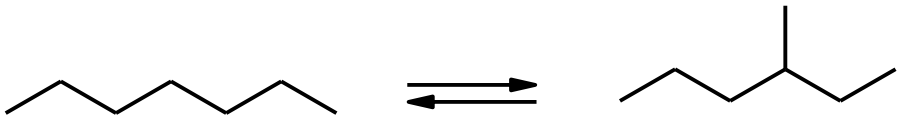
Specific gravity, g/cm3	0,6838	0,8669
RON:	0	119,7

Main reactions 2.

Isomerisation

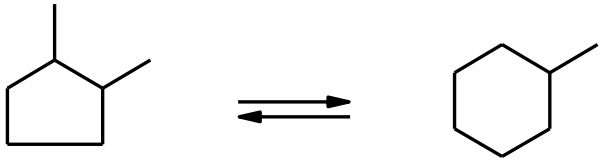
$\Delta H = -4{,}4$ kJ/mol

n-paraffin → i-paraffin



Specific gravity, g/cm3	0,6838	0,6871
RON:	0	52,0

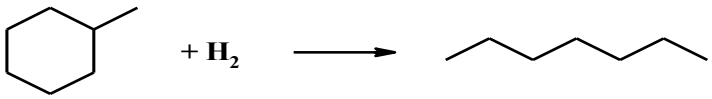
C5 cycloparaffin → C6 cycloparaffin

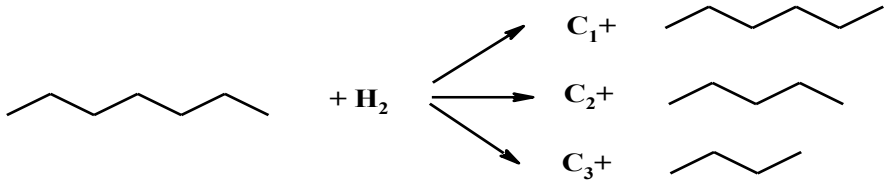


Specific gravity, g/cm3	0,7913	0,7694
RON:	100,4	73,8

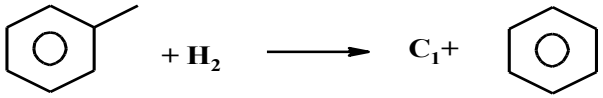
Side reactions

Hydrocracking

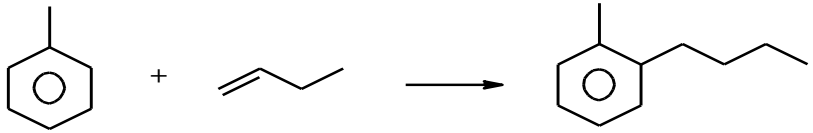




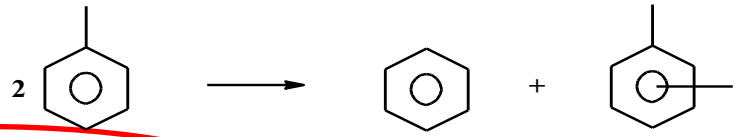
Hydrodealkylation



Alkylation

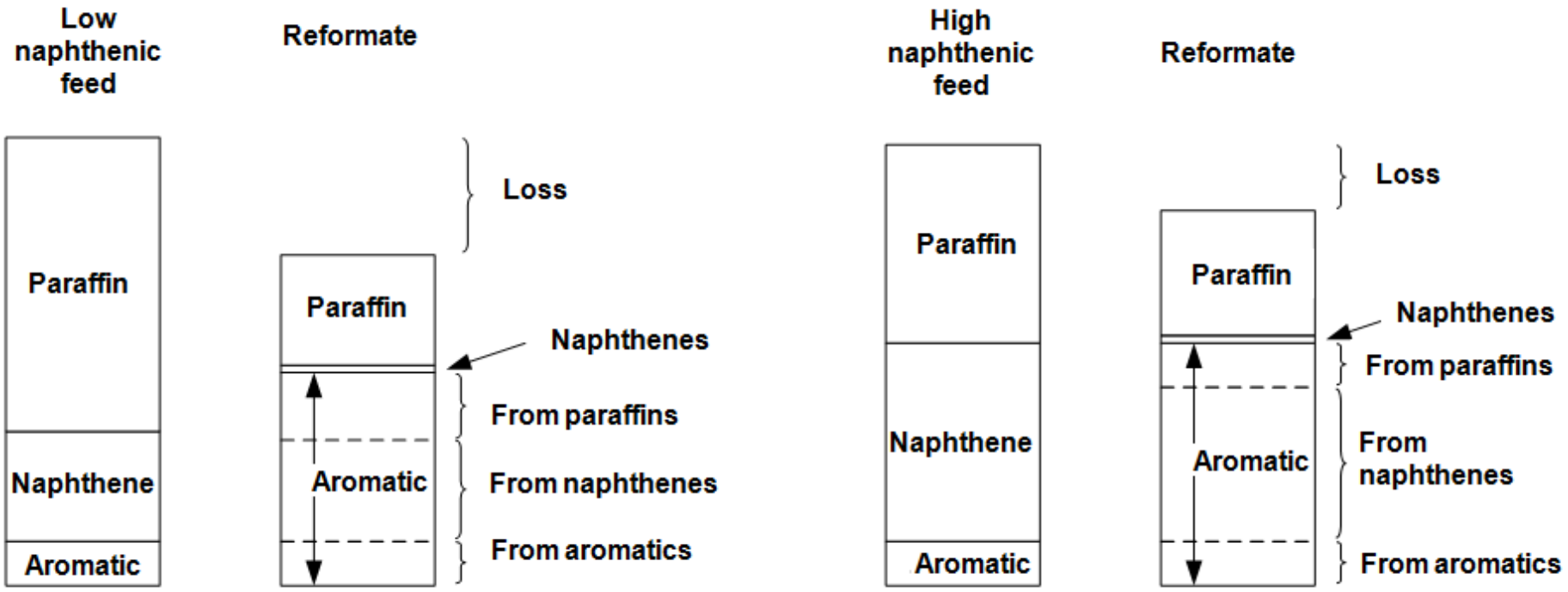


Disproportioning



Coke formation

Volume-yield correlation



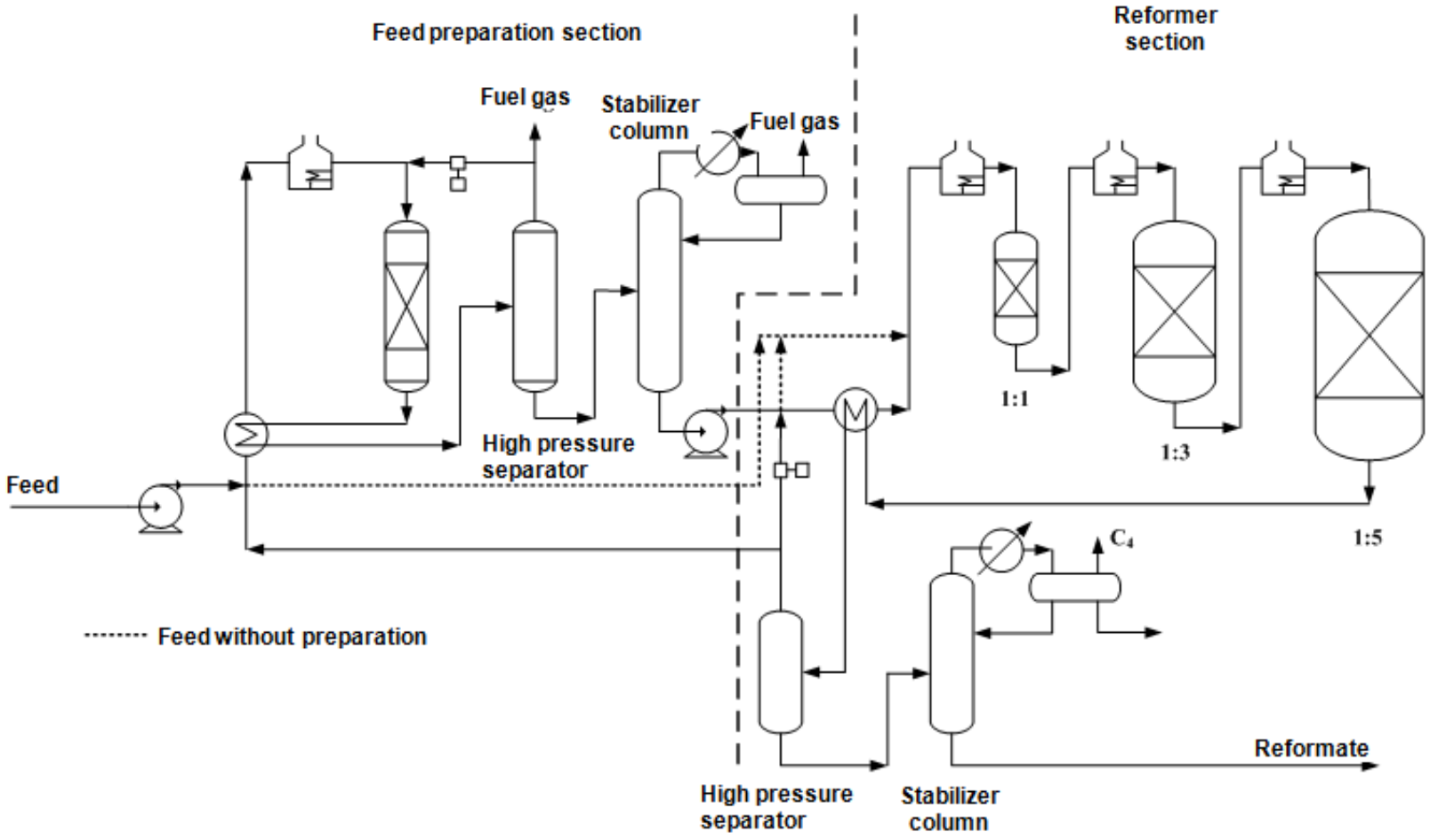
- Specific gravity of the product is **significantly higher** than the feed specific gravity

Process parameters

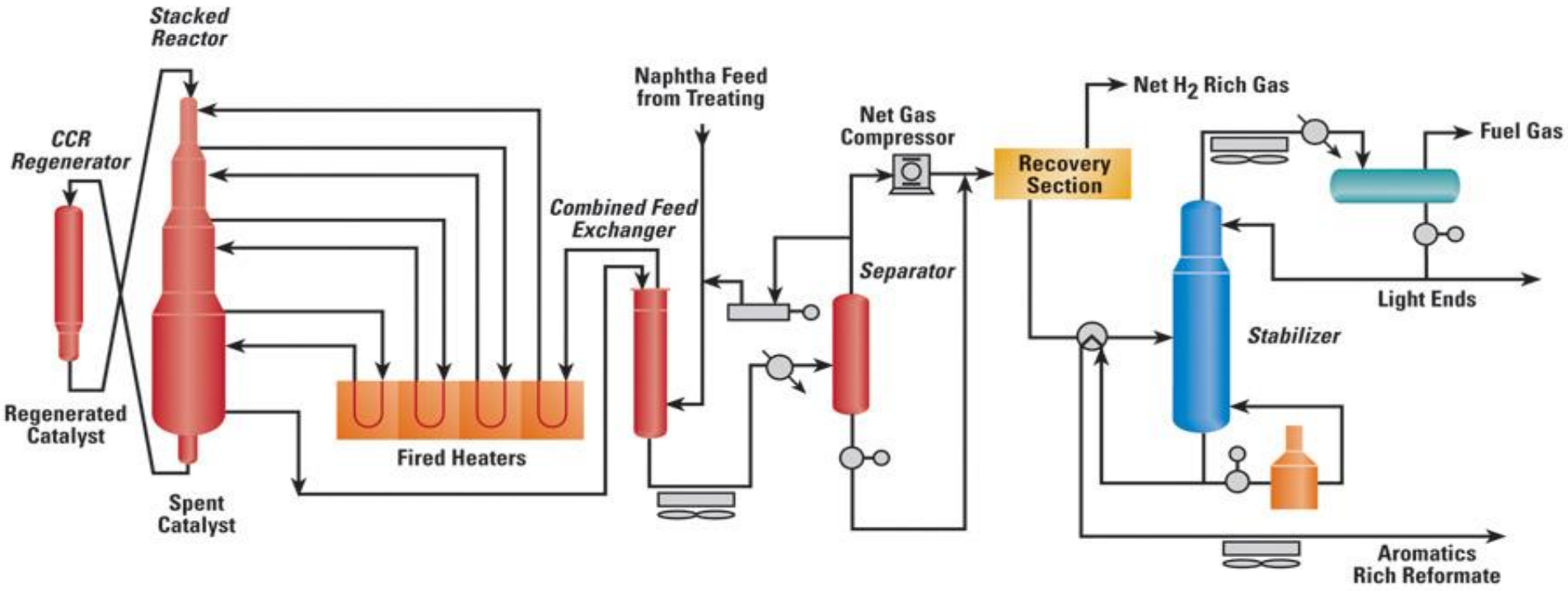
- **Temperature:** 480-520 °C
- **Pressure:** 5-8 bar vs. 20-30 bar
- **Liquid load:** 1,5-3,0 M3/m3h
- **H2/hydrocarbon mol ratio:** 5:1 – 12:1
- **Catalyst:** bifunctional, bimetallic
  - Hydrogenation-dehydrogenation function
    - Platinum (main component)
    - Rhenium, tin, etc. (stabilizes the platinum, selectivity increases)
  - Isomerization function
    - Acidic support (γAl_2O_3)

Obsolete solution:

fixed bed process



BAT solution:
moving bed process (CCR)



- **BAT: B**est **A**vailable **T**echnology
- **CCR**: **C**ontinuous **C**atalyst **R**egeneration

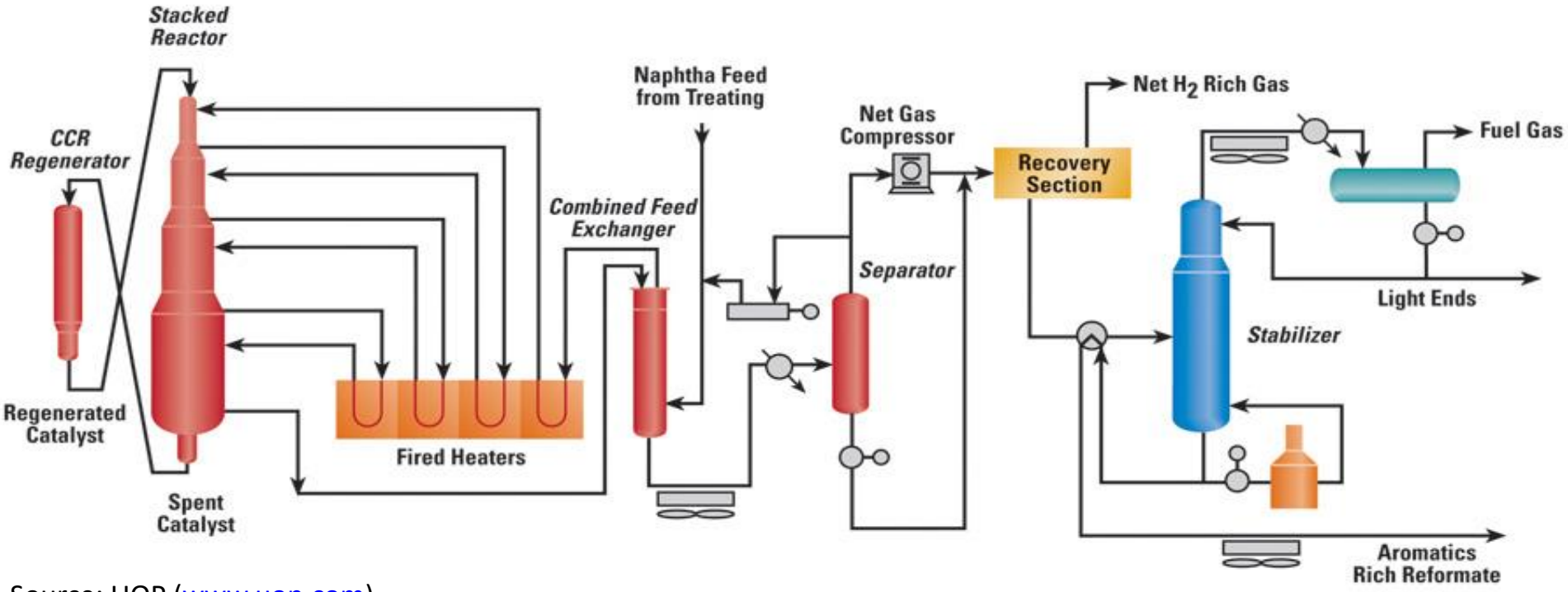
Source: UOP (www.uop.com)

Advantages of CCR process

- Lower **pressure**
  - Smaller operational cost (OPEX)
  - Reaction equilibrium pushed towards products
- **Continuous** operation for 4-5 years
  - No production loss
- Higher catalyst **activity**
  - Better selectivity (more aromatic products)
  - More hydrogen
  - Higher octane number (RON 102-105)

CCR reforming

- **Aim:** Production of high octane gasoline blending component
- **Feedstock:** heavy naphtha
- **Process parameters:** ~500°C, 8 bar
- **Heat balance:** endothermic
- **Catalyst:** Pt-Re/Al_2O_3
- **Products:** reformate, hydrogen, benzene rich fraction



Source: UOP (www.uop.com)

3. Etherification, oxygen containing compounds

Alcohols

1. melléklet a 17/2017. (V. 26.) NFM rendelethez

A forgalmazott motorbenzin minőségi követelményei

9	Szénhidrogén-összetétel:			
10	- Olefintartalom	% (V/V)	-	18,0
11	- Aromás anyag-tartalom	% (V/V)	-	35,0
12	- Benzoltartalom	% (V/V)	-	1,0
13	Oxigéntartalom	% (m/m)	-	3,7
14	Oxigenátok:			
15	- Metanol (stabilizáló adalékok hozzáadása szükséges)	% (V/V)	-	3
16	- Etanol (stabilizáló adalékok hozzáadására lehet szükség)	% (V/V)	-	10
17	- Izopropil-alkohol	% (V/V)	-	12
18	- Tercier-butil-alkohol	% (V/V)	-	15
19	- Izobutil-alkohol	% (V/V)	-	15
20	- Molekulánként öt vagy több szénatomot tartalmazó éterek	% (V/V)	-	22
21	- Egyéb oxigenátok [az MSZ EN 228:2012 szabvány szerinti értéknél nem magasabb végső forráspontú egyéb monoalkoholok és éterek]	% (V/V)	-	15
22	Kéntartalom	mg/kg	-	10

- In practice: **alcohol ~ bioethanol**

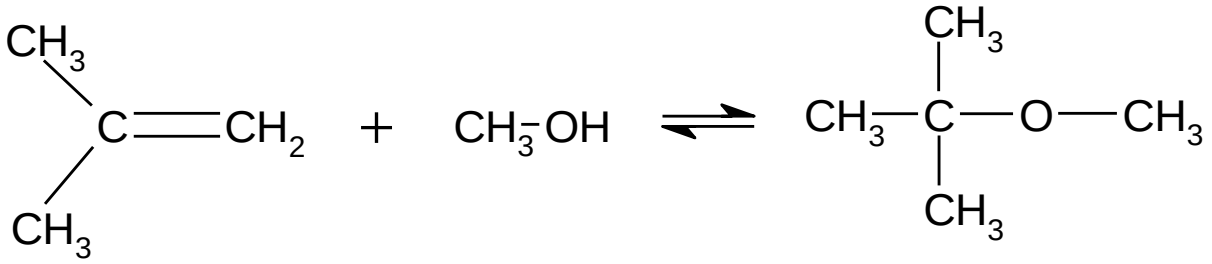
Ethers

Parameters	MTBE	ETBE	TAME
Boiling point, °C	55,2	71,7	86,1
Flash point, °C	-28	-19	-11
Oxygen content, %	18,2	15,7	15,7
Research octane number (RON)	**118**	**118**	110
Motor octane number (MON)	100	102	97
Water solubility ether in water, v/v % water in ether, v/v %	 4,3 1,4	 2,0 0,6	 0,6 0,6

- **ETBE**: **E**thyl-**T**erciary-**B**uthyl-**E**ther
- In practice: ethanol from corn (bio)

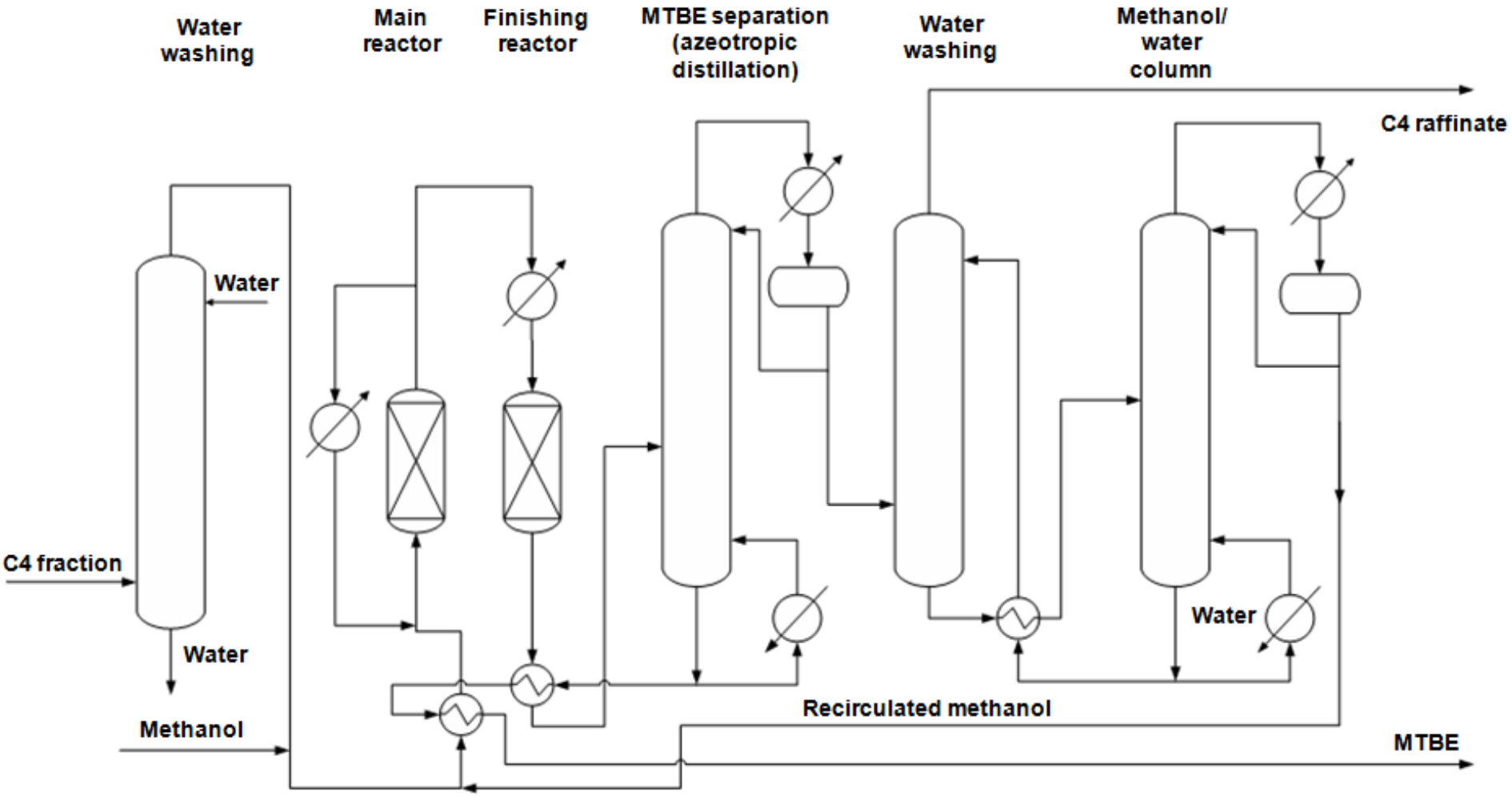
Etherification: **process parameters**

- **Catalyst:** acidic ion exchange resin (relatively cheap)
- Feed: olefinic C4 mixture (iso-butylene), alcohol
  - Tertiary olefins will selectively react with alcohol, while the rest leaves the reactor without any reaction
  - Simple alcohols are used (MeOH, EtOH)
  - Since the bio-component regulation, mainly bio-ethanol
- **Reaction:**



- **Heat balance:** exotherm reaction, ~ 37 kJ/mol reaction heat
- **Temperature:** 50-90°C in the main reactor, 40-60 °C in the finishing reactor
- **Pressure**: 7-20 bar
- LHSV (space velocity): 4-6 m^3/m^3h
- Ethanol/isobutylene molar ratio: 1,1-1,2

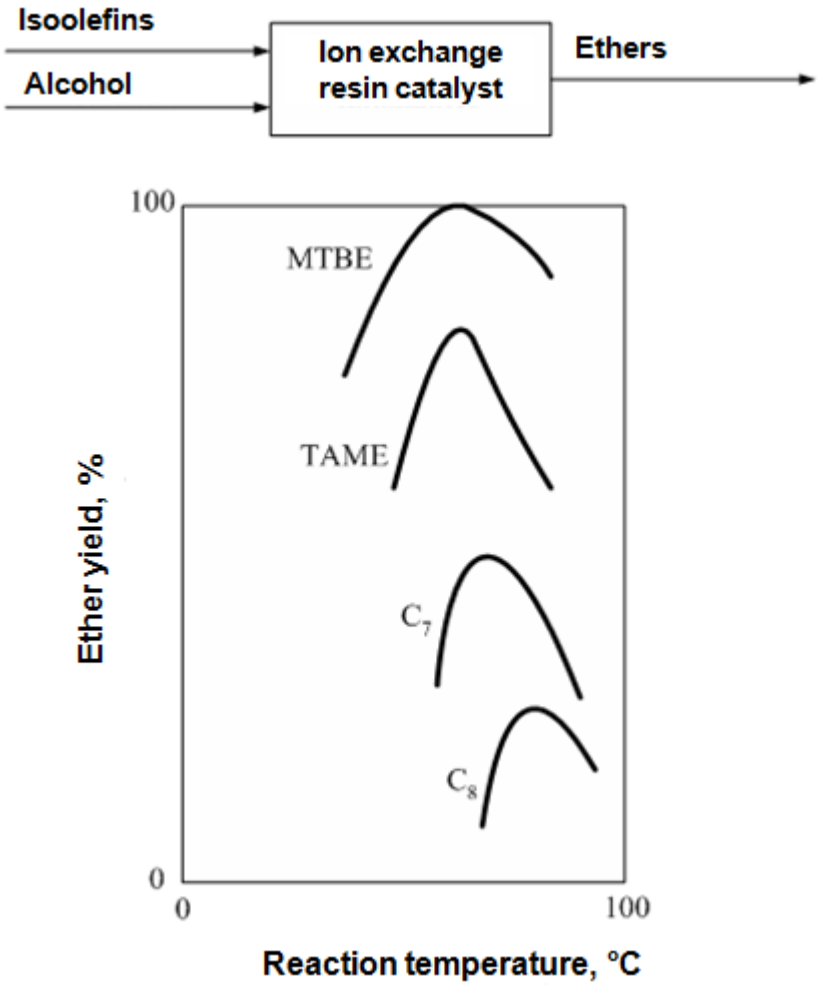
Etherification **flowscheme**



- Water washing is executed by **ionfree water** (caustic traces from MEROX process and alcohol surplus reuse)

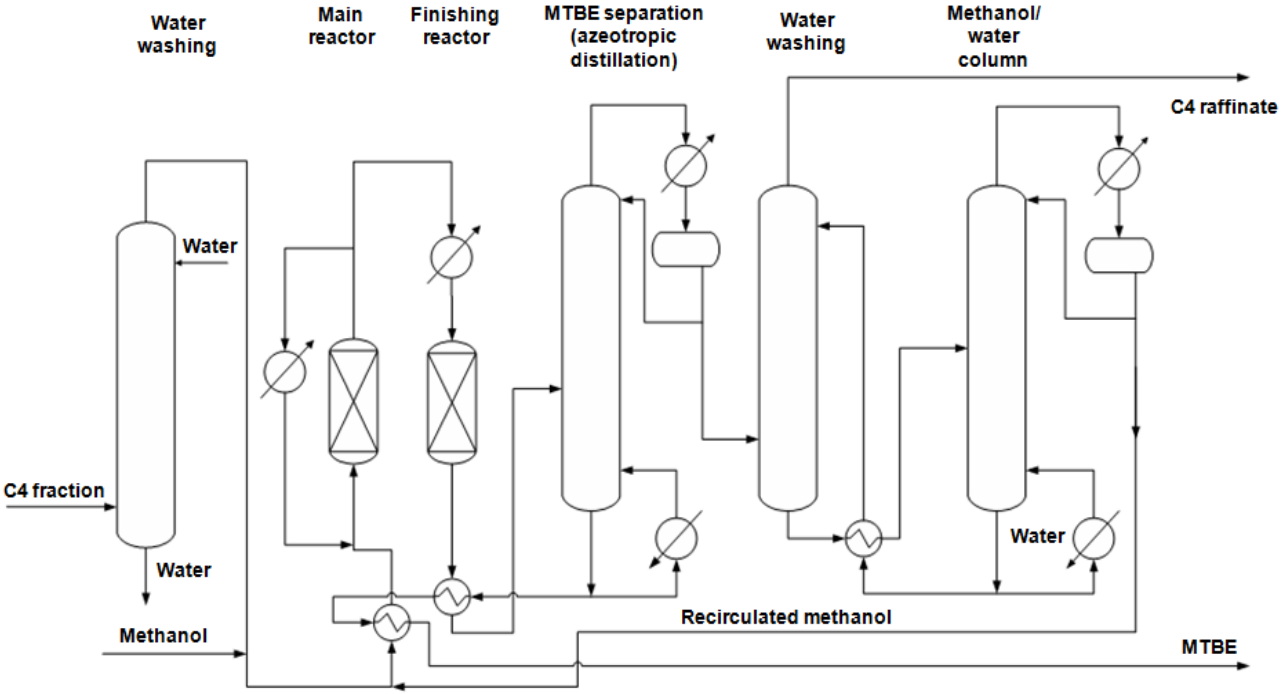
Why do we use mainly C_4 olefins?

- The C_3 olefin do not contains tertiary carbon atom, and the propylene **could be sold at high price**
- Separation of C_6 and heavier olefins are **costly**
- **Ether yield is reduced significantly** along the carbon number increase



Etherification

- **Aim:** production of high octane (bio) oxygenate
- **Feedstock:** olefinic C_4 fraction (isobutylene), (m)ethanol
- **Process parameters:** 50°C, 20 bar
- **Heat balance:** highly exothermic
- **Catalyst:** highly acidic ion exchange resin
- **Products:** MTBE/ETBE, C_4 raffinate (incl. other C_4 olefins)



4. Alkylation

Chemistry of alkylation

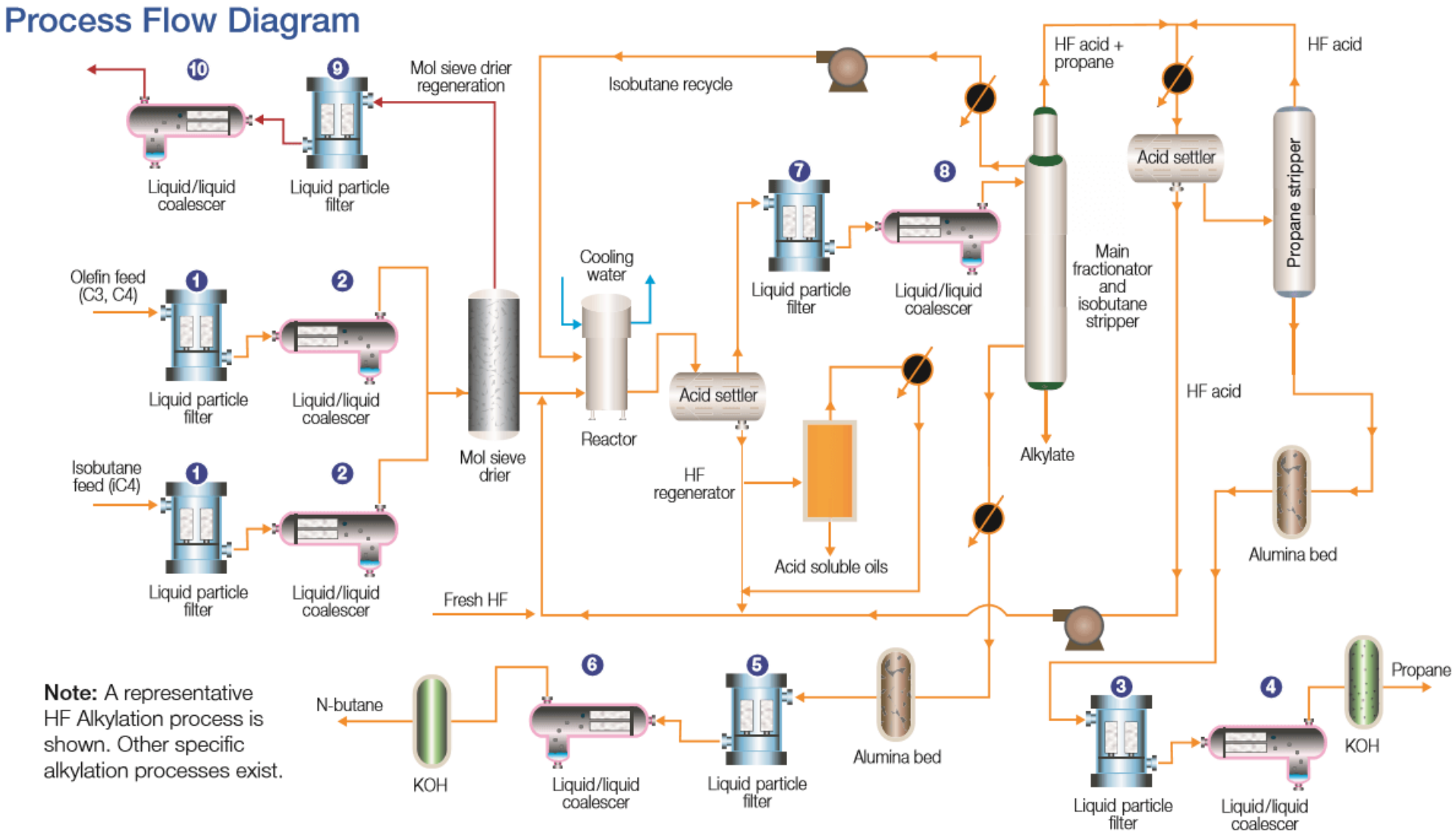
- **Reaction:**
  - Feed: i-butane + ($C_{3=}$)/**$C_{4=}$**/($C_{5=}$)
  - catalyst: **HF** or H_2SO_4
  - **Homogeneous catalytic** process
  - Product: alkylate gasoline
- **Mechanism:** via carbenium ion
- **Heat balance:**
  - Highly exotherm (-480 – -630 kJ/kg alkylate)
  - Heat removal is important
- At higher temperature **polymerisation side reactions** will start, which result in higher boiling point product (yield and octane-mass loss)

Process parameters of alkylation

Parameter	HF	H_2SO_4	Solid acid
Reactor temperature, °C	**25-45**	**6-10**	100-250
Pressure, bar	20	15	20-50
Isobutane:olefine ratio, V/V	15-20	10-15	5-8
Acid concentration, %	**58-90**	**98-99**	-
Acid in the mixture, %	50-70	50-75	-
Acid consumption, kg/t alkylate	**0,4-0,7**	**35-150**	-

- **Advantages of HF process**
  - Ideal reaction temperature (see cooling water temperature around ~20-25°C)
  - Concentrated acid is not needed
  - Low acid consumption (minimum harmful waste)
- **Drawbacks of HF process**
  - Very dangerous acid

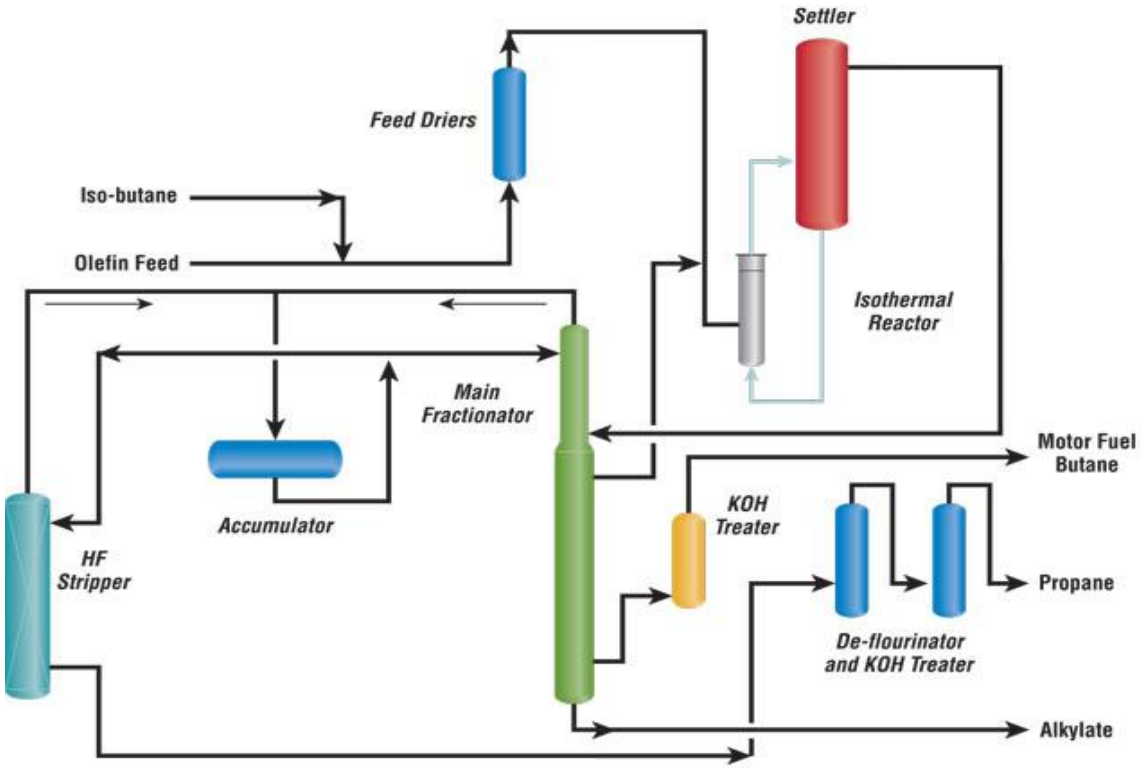
Alkylation: process flow diagram



Source: https://www.pall.com/en/oil-gas/refining/refinery-alkylation.html

(HF) Alkylation

- **Aim:** production of aromatic free gasoline blending component
- **Feedstock:** olefinic C_4 fraction, olefinic C_3 fraction and i-butane
- **Process parameters:** 30°C, 2-5 bar
- **Heat balance:** exothermic
- **Catalyst:** HF acid (or H_2SO_4 in case of Sulphuric acid alkylation)
- **Products:** alkylate, n-butane, propane



The End

Forrás: https://www.archdaily.com/926414/what-is-the-future-of-the-gas-station