Hydrocarbon processing

Refinery products, products blending

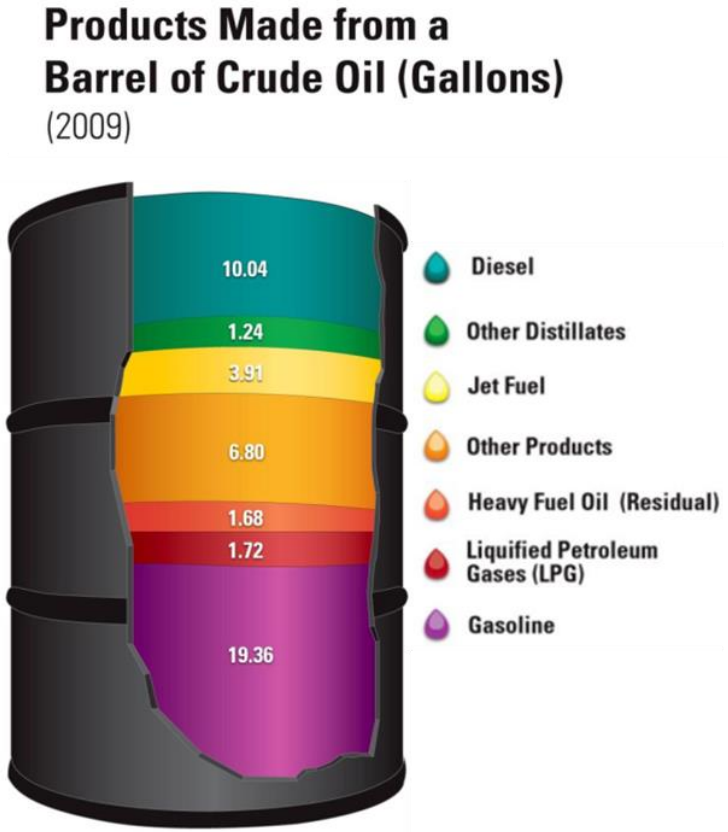
English version based on the presentation
of Dr. Márton Krár held on 02.10.2013

Agenda

- Refinery products
- Motor gasolines
  - Blending components
  - Additives
- Diesel gasoils
  - Blending components
  - Additives
- Blending of motor fuels
  - Blending types
  - Information necessary for blending
  - The blending process
  - Main units of a blending plant

Product types

- Gases (LPG, PB)
- Aviation (JET A1, aviation fuel)
- MoGas (E5/ESZ95, EVO NEO)
- Diesel (B7, EVO)
- Heating oils / non road diesel
- Base oils (for lubricants)
- Fuel oils (electricity, bunkering)
- Paraffin waxes (micro-, macroparaffins)
- Bitumen (paving-, modified bitumen)
- Aromatics (benzene, toluene, xylenes)
- Special spirits, solvents
- Petrochemical and other products (sulphur, petrol coke, Maleic acid anhydride)



Source: USA - energy.gov

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- LUB and PETCHEM product portfolio

Refinery Product Classifications

- Finished Products
  - Ready for use by refinery costumer
- Unfinished Products or Intermediates
  - Need more processing or blending with other materials
    - Naphtha (light and heavy) to petrochemicals
    - Straight Run Atmospheric Residue
    - Vacuum Gas Oil (VGO)
    - Blend stocks
- Own Use or Internal Use Products
  - Refinery liquid fuel oil
  - Refinery fuel gas
- Major Refinery Products
  - Gasoline, kero/jet, Diesel, Fuel oils

Gases (LPG)

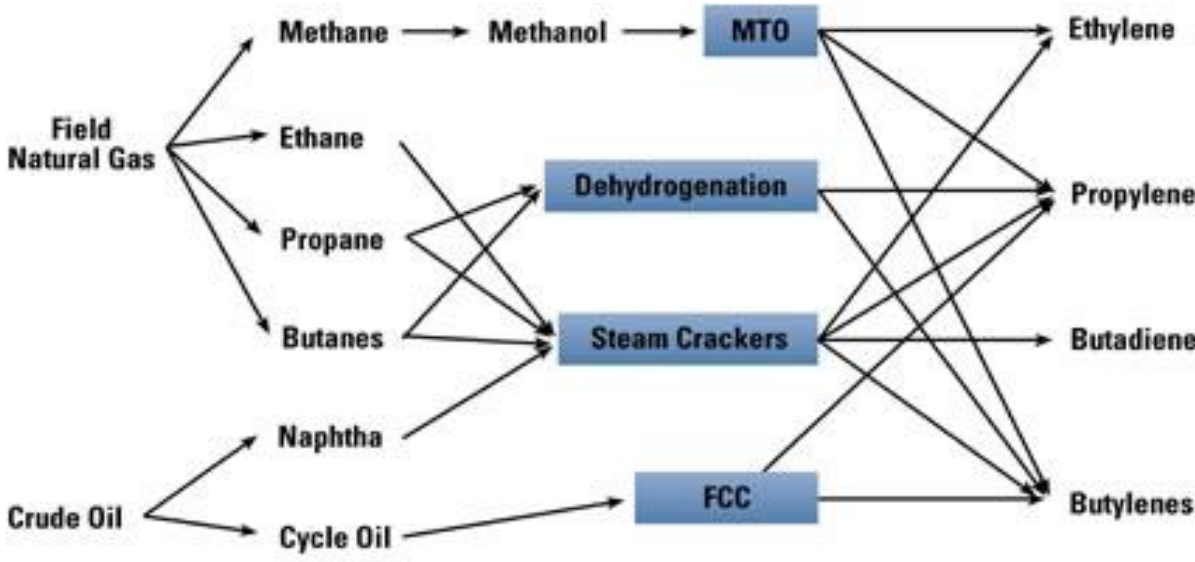
- Produced from saturated and unsaturated C3 and C4 gases
- Sales
  - LPG – mixed C3's and C4's
  - Butanes (iso, normal or mix)
  - Petrochemical Feed (propylene/butylene)
- Stronger market typically in winter
- Production vs. alternative utilization
  - Butane/butylene to gasoline
  - Propylene/butylene as Cat Poly/Alky/MTBE Feed
  - Refinery fuel or Hydrogen Manufacturing Unit Feed

Gasoline

- Used as fuel for Spark-Ignition Internal Combustion Engines
- Blend of several naphtha range streams, C4s, and in some cases oxygenates
- Stronger market in summer
- Production vs. alternative utilization
  - C4s to LPG
  - Gasoline to virgin naphtha or aliphatic solvent feed
  - Heavy naphtha to kerosene
  - Light Reformate to aromatics feedstock
  - Heavy FCC Naphtha to Diesel/Heating Oil/Fuel oil

Petrochemical Feeds

- Petrochemical Feeds
  - Propylene
  - n-butane
  - BTX
  - Virgin naphtha
  - Petrochemical gasoil
  - Sulphur



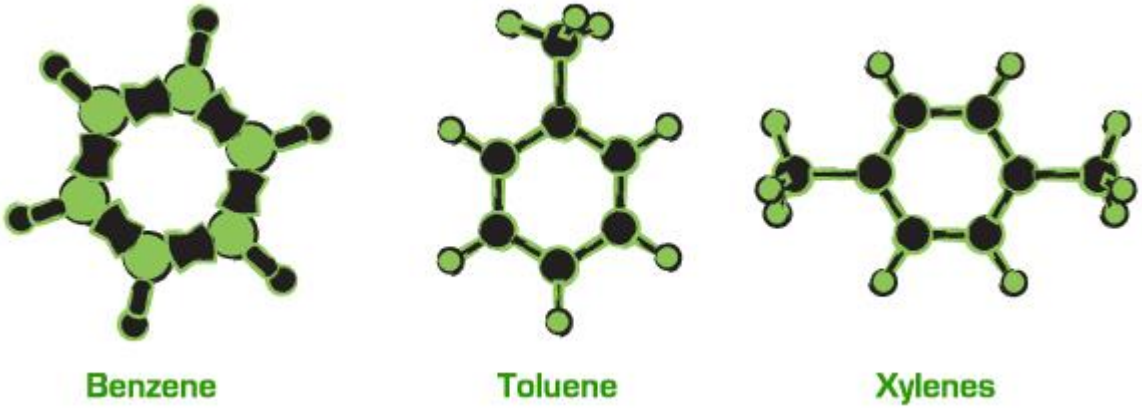
- Specifications
  - Typically composition or distillation specific
- Production vs. alternative utilization
  - C3s- LPG
  - C4s- gasoline/LPG
  - Naphtha- gasoline production
  - Gasoil - Diesel production

Aliphatic solvents

- **Solvents – Produced from naphtha streams**
  - **Aliphatic gasoline fractions obtained in crude oil refining are subjected to aromatic removal process in a catalytic reaction. A solvent of low aromatics and sulphur contents.**
  - **Field of application: production of thinners, lacquers, paints, washing down oily surfaces**

Aromatics

- Benzene, Toluene and Xylenes (BTX) sold as feedstock to Petrochemical Industry
- Produced from Light Reformate, petrochemical aromatics
- Specifications – Composition
- Production driver vs. alternative utilization
  - Gasoline blend stock



Kerosene/Jet Fuels

- Jet Fuels (Jet A1, JP8 and JP5)
  - Jet A1 – Commercial airline
  - JP8/JP5 Military
- Stronger market in summer
- Kerosene (Lamp oil) – Typically small amount
- Production vs. alternative utilization
  - Diesel/Heating oil
  - Solvents

Diesel/Heating Oil

- Grades
  - Auto/off road Diesel
  - Military Diesels
  - Heating Oil
  - Marine Diesels
- Auto Diesel stronger market in summer
- Heating Oil stronger market in winter
- Production vs. alternative dispositions
  - Kerosene/Jet
  - Petrochemical gasoil

Fuel Oil

- Used for fuel in Power Generation on Ships (Bunker)
- Grades
  - High Sulphur Fuel Oil
  - Low Sulphur Fuel Oil
  - Light Fuel Oil
  - Heavy Fuel Oil
  - Bunkers
- Fuel oil is mixture of the heavy streams (Vacuum Residue, FCC MCB)
- Alternative disposition
  - Feed for residue upgrade units e.g. cooker feed
  - Asphalt
  - Front end Vacuum Residuum to Cracking
  - Base oil production

Bitumen

- Used for mainly road construction, isolation, roofs
- Bitumen is a Vacuum Residuum
  - Crude is key factor in production
- Specifications
  - Penetration - Amount material yields to a weight dropped on it at 25 °C
  - Softening Point – Temperature which asphalt starts to lose its resistance to flow
- Alternative dispositions
  - Coker feed
  - Fuel Oil

Paraffin

- **Used for/by**
  - **Candle production, paper production, wood industry, match industry, rubber industry, cosmetics industry, agriculture, food industry, casting wax, etc.**

- **Specifications**
  - **Paraffin wax is mostly found as a white, odorless, tasteless, waxy solid, with a typical melting point between about 47 °C and 64 °C**

Base Oils

- Base oil is the main raw material of lubricants
  - It is produced with vacuum distillation.

- Specifications
  - MOL base oils meet the most-up-to-date international requirements in terms of performance properties and classes of viscosity and they can be used in motor oil and industrial oil production as well.

Other Products

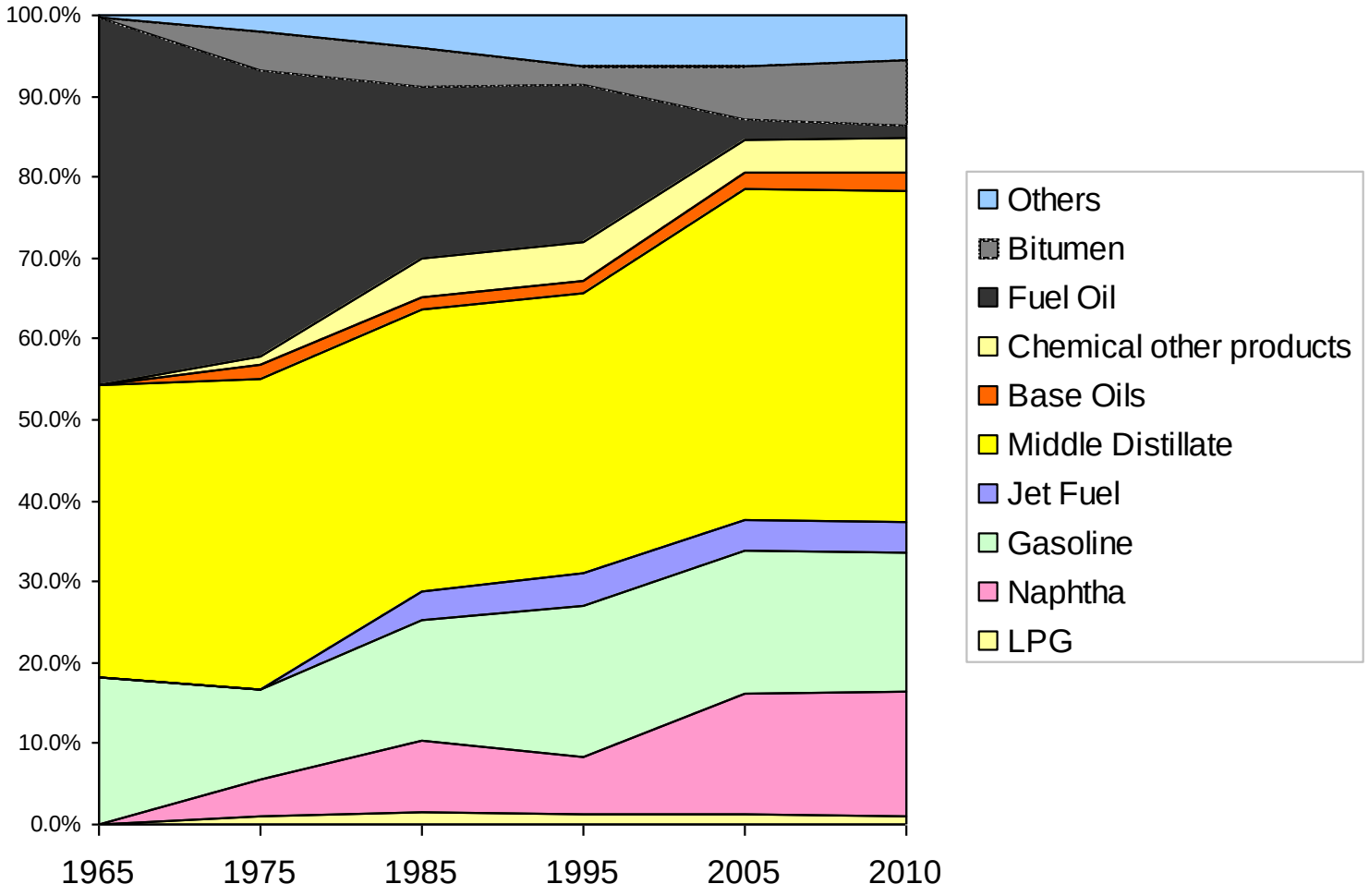
- **Maleic Acid Anhydride**
  - **Used as a base material of unsaturated polyester resins**

- **Sulphur**
  - **Elemental sulphur is mainly used as a precursor to other chemicals**

Other Products

- **Petroleum Coke**
  - **Solid product with high caloric value can be sold only for industrial end users**

Huge Changes in yield structure ... (DR)



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  - Blending components
  - Additives
- Diesel gasoils
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- Blending of motor fuels
  - Blending types
  - Information necessary for blending
  - The blending process
  - Main units of a blending plant

Glossary of basic terms – I.

Blending components

- Final products of different crude oil processing steps

Additives

- From synthetic or natural sources, low concentration (< 0,1%)
- Improvement of a given property or a new property introduction
- Motor constructors & end users: high quality requirements
- Help to reach standardized properties & to improve value

Fuel standards

- Quality parameters + standardized measurements
- EU standards valid since 1999 in Hungary

Glossary of basic terms – II.

Motor gasoline

- Liquid hydrocarbon product, boiling up to 210°C. Components derived from crude oil and/or artificial hydrocarbon atmospheric distillation, thermal cracking or catalytic reshaping. Motor gasoline is a mixture of paraffin, naphthene and aromatic hydrocarbons, boiling in the range of 50-210°C

Octane number (RON)

- Octane number is the measure of compression resistance of gasoline. It is equivalent to the isooctane content (vol%) of the isooctane (RON=100) and n-heptane (RON=0) mixture, which has the same compression resistance as the sample in question, under standardized measuring conditions.

Compression resistance

- Behaviour of motor fuels, which shows the extent of pressure and temperature durability under operating conditions, without the sudden speed-up of speed of burning, which is causing knocking.

Glossary of basic terms – III.

Diesel gasoil

- heavier fraction of different hydrocarbon mixtures, formed during atmospheric distillation, fuel of the Diesel engine. 95% will be distilled off below 360°C. In case of the Diesel engines, the combustion air is compressed within the cylinder which will warm up due to the compression. The diesel gasoil is sprayed into this warm air. This must get ignited by itself and keeping burning during the whole evaporation period. The high quality gasoil is comprised of paraffins instead of aromatics. Burning behaviour is characterised by cetane number.

Cetane number

- value characterising the self-ignition ability of gasoils. It is equivalent to the n-cetane content (vol%) of the n-cetane (Cet.number=100) and alpha-methyl-naphthalin (Cet.number=0) mixture, which has the same compression resistance as the sample in question, under standardized measuring conditions.

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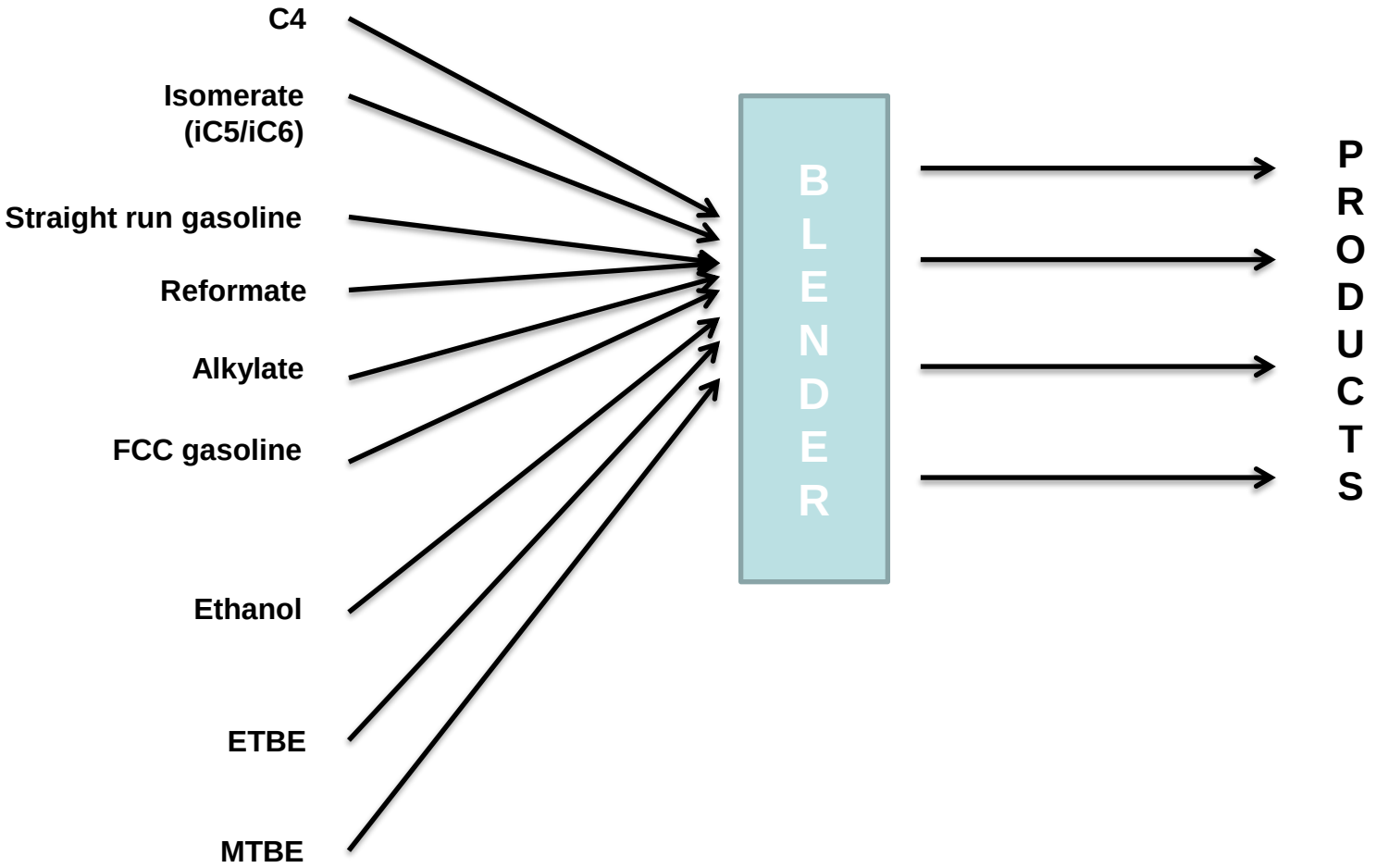
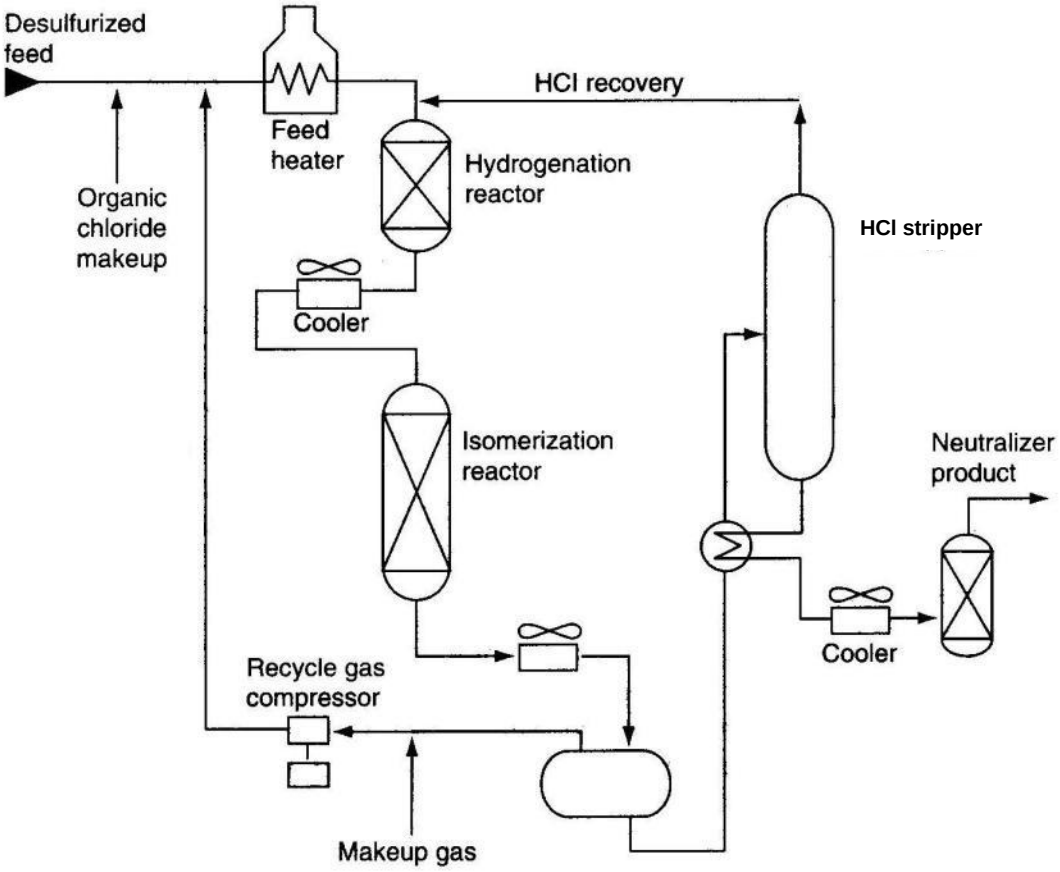
Motor gasoline blending – blending components



Light naphtha isomerisation



Goal: high octane blending component production

Feedstock: n-C_5 – n-C_6

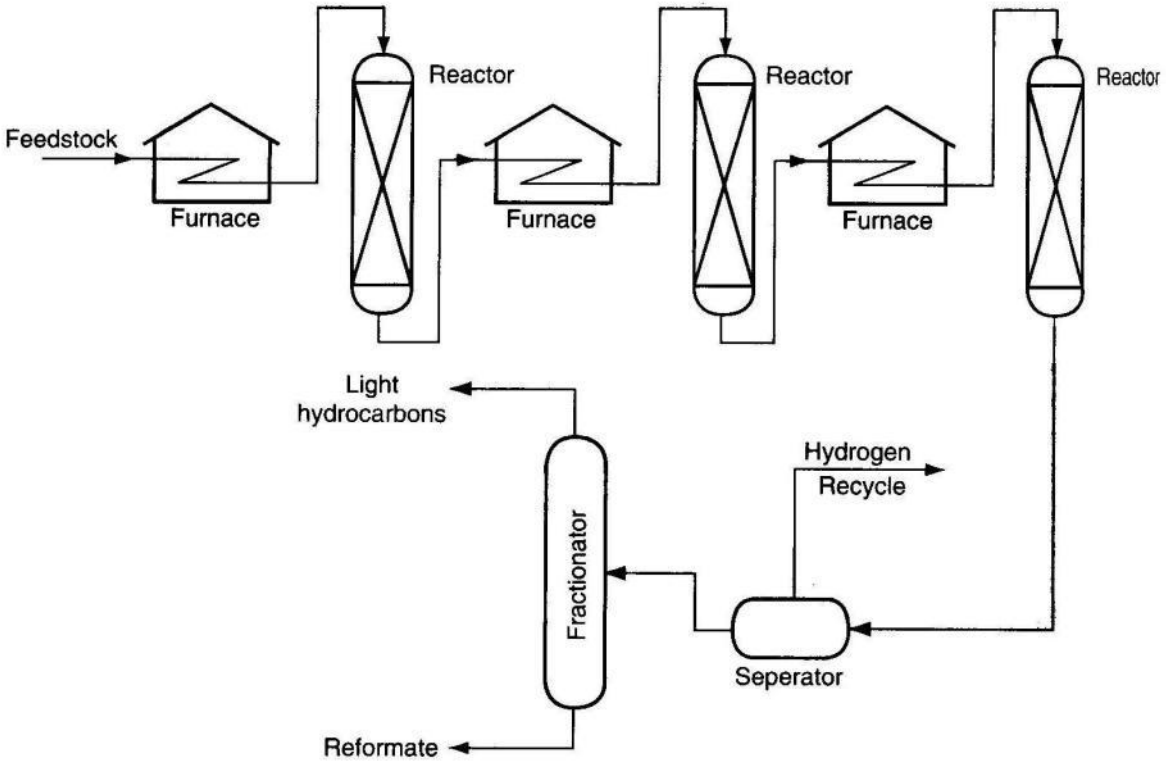
Product: isomerised C_5 – C_6

Process parameters:

- **Temperature: 40 - 480 °C**
- **Pressure: 10 – 70 bar**

Catalyst: Pt – Al_2O_3 – Cl, Pt – zeolite

Reforming



Goal: high octane blending component production, individual aromatics (BTX) and hydrogen production

Feedstock: desulphurised heavy naphtha

Product: reformate, hydrogen, BTX

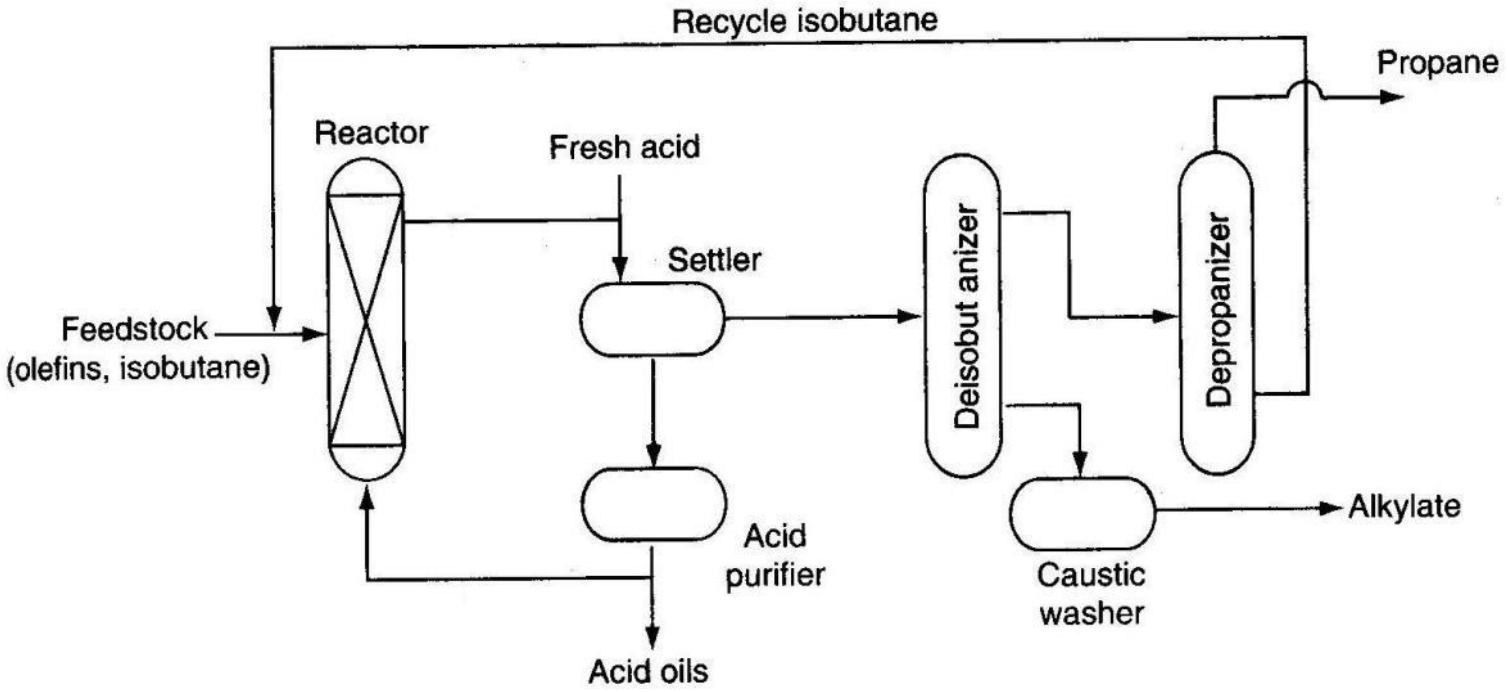
Process parameters:

Temperature: 450 - 550 °C

Pressure: 45 – 50 bar

Catalyst: Pt-Re – Al_2O_3 / zeolit–Cl

Alkylation



Goal: production of high octane isoparaffins via reaction of iso-butane and butenes

Feedstock: isobutane + butenes

Product: Alkylate

Process parameters:

Temperature: 1 - 40 °C

Pressure: 1 – 10 bar

Catalyst: H_2SO_4; HF

FCC (Fluid Catalytic Cracking)

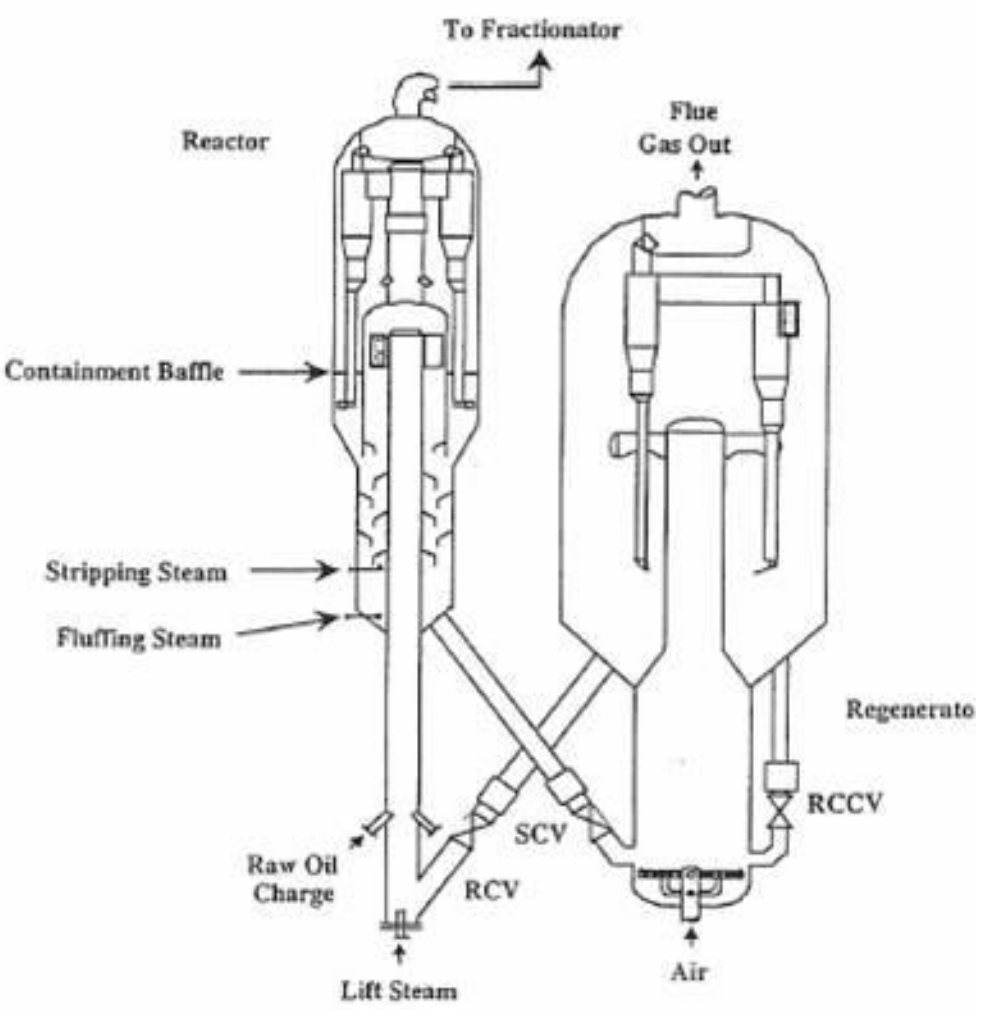
Goal: production of lighter fractions via controlled cracking

Feedstock: desulphurised HVGO

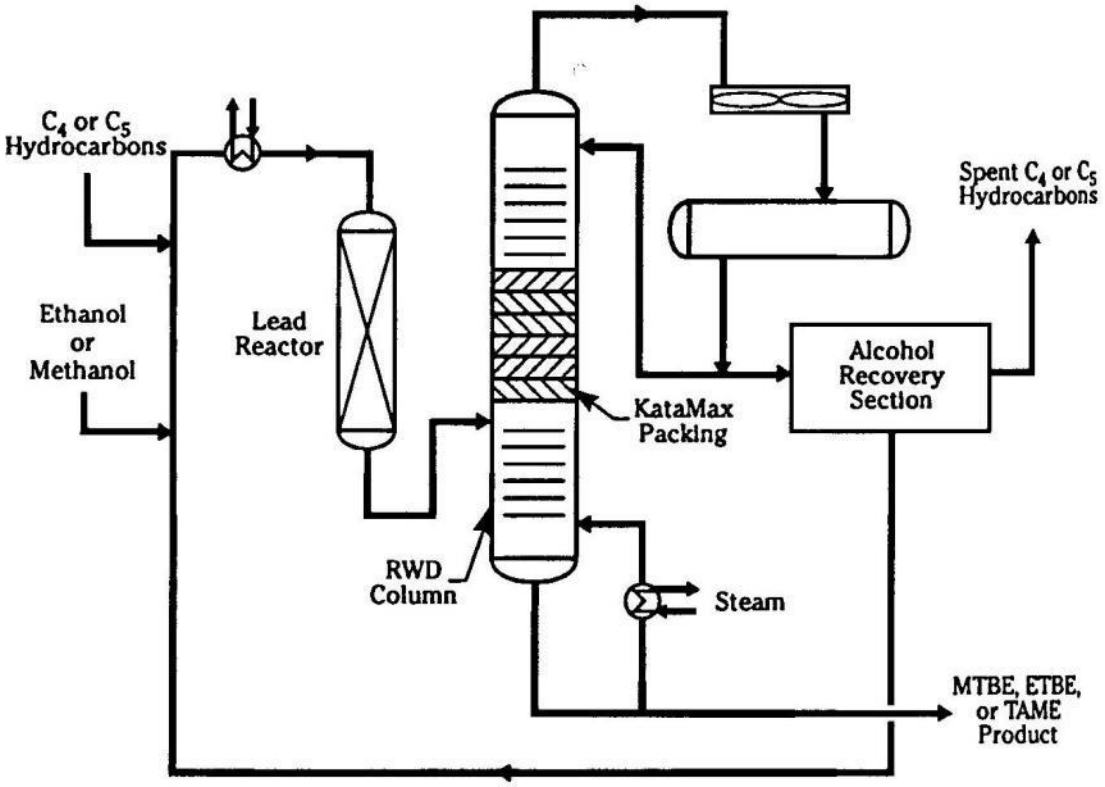
Product: LPG, FCC gasoline, LCO

Process parameters:

- **Temperature: 480 - 540 °C**
- **Pressure: 2 – 4 bar**
- **Catalyst:**
  - **zeolitok (Al_2O_3 - SiO_2)**



MTBE/ETBE



Goal: Production of high octane blending component (from partially bio sources)

Feedstock: C_4-olefin mixture (isobutene) + methanol/ethanol

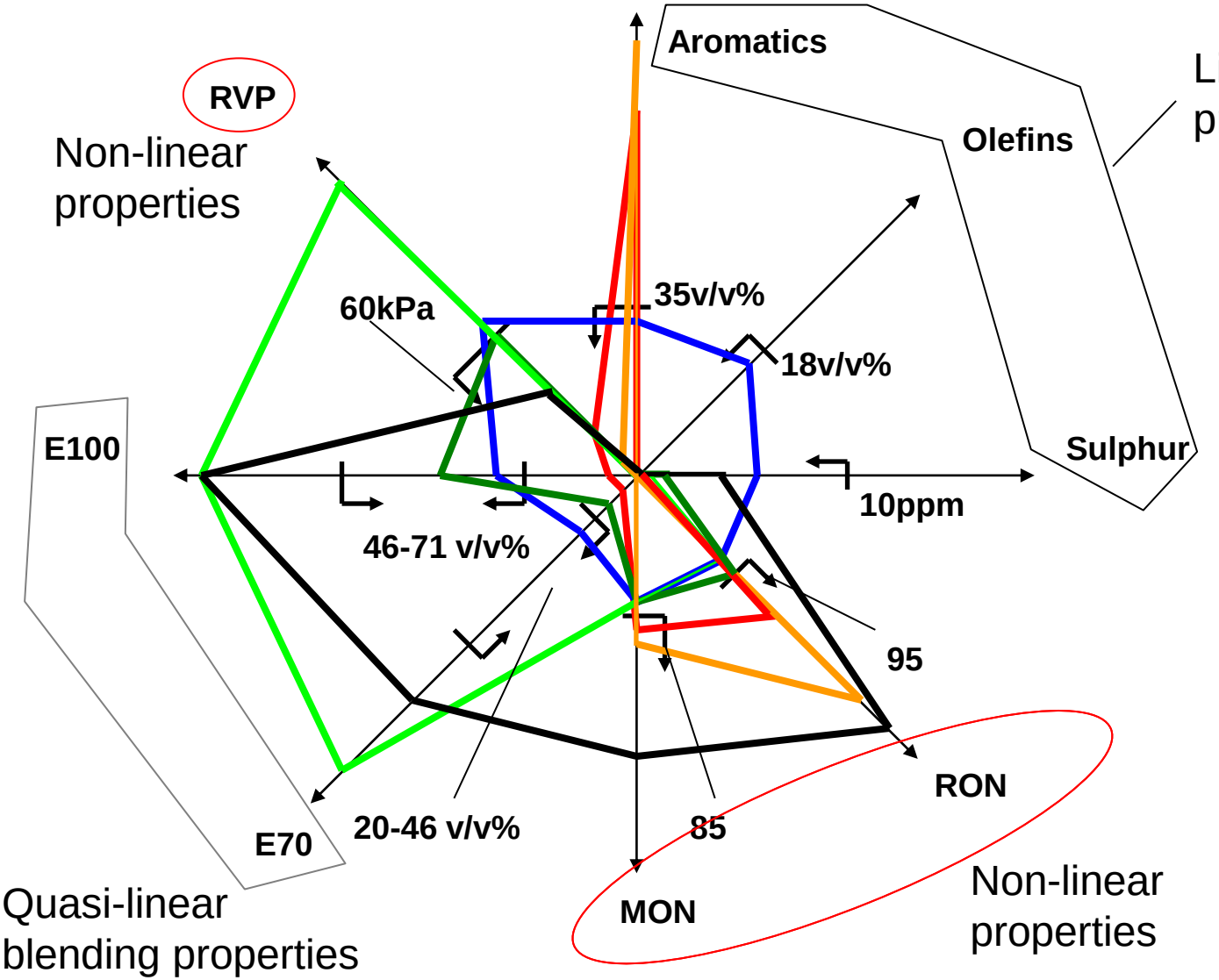
Product: MTBE/ETBE

Process parameters:

- **Temperature: 50 - 60 °C**
- **Pressure: 14 – 17 atm**

Catalyst: ion exchange resins

Motor gasoline blending – blending properties



Blending bonuses

Blending bonuses

Motor gasoline blending – additives I.

Additive	Requirement/effect/achievement	Active agent	Additive concentration, ppm
Octane booster	Increase of octane number	Metal containing: MMT, Tetraethyl lead	5-20
		Ash less: aniline, alcohols ethers	10-1000
Detergent-dispergent	Clean up and keep clean (injector, carburetor inlet and outlet system)	Alkenyl succinimides, polybuteneamines, polyetheramines	20-70
Corrosion inhibitors	To protect fuel system against corrosion	Esters or amine salts of alkenyl succinic acids, alkylortho-phosphoric acids, alkyl phosphoric acids, aryl sulfonic acids	5-20
Anti-icing additives	To prevent ice formation in the carburetor or throttle body	Alcohols, glycols	10-30
Antioxidants	Improving the storage stability and prevent gum formation	aromatic diamines	5-20
		alkyl phenols	5-100
		these mixtures	5-100
Metal deactivators	Deactivate metals (such as copper) which are catalyzing oxidation reactions	N,N'-disalicylidene-1,2-propanediamine	4-12
Combustion improvers	Lower emission (catalytic effect on the combustion process)	Ferrocene	1-10

Motor gasoline blending – additives II.

Additive	Requirement/effect/achievement	Active agent	Additive concentration, ppm
Friction modifiers & anti-wear additives	**Lubrication of upper cylinder and minimize engine friction in the**	**Molybdenum-based additives, saturated fatty acids, esters**	**80-200**
Anti-valve-seat recession additives	**Phase out of lead occurred valve seat recession on engines having “soft” valve seat. Eg.: lubrication of outlet valve seats**	**Sodium or potassium containing additives**	**50-200**
Anti ORI (octane requirement incrase)	**To prevent the increase in octane requirement occurred by lay down deposits in the combustion chamber**	**polyetheramines**	**20-200**
Antistatic additives	**To improve the electrical conductivity of the gasoline**	**total organic type additive or water soluble oxygenates as blending component**	**2-10**

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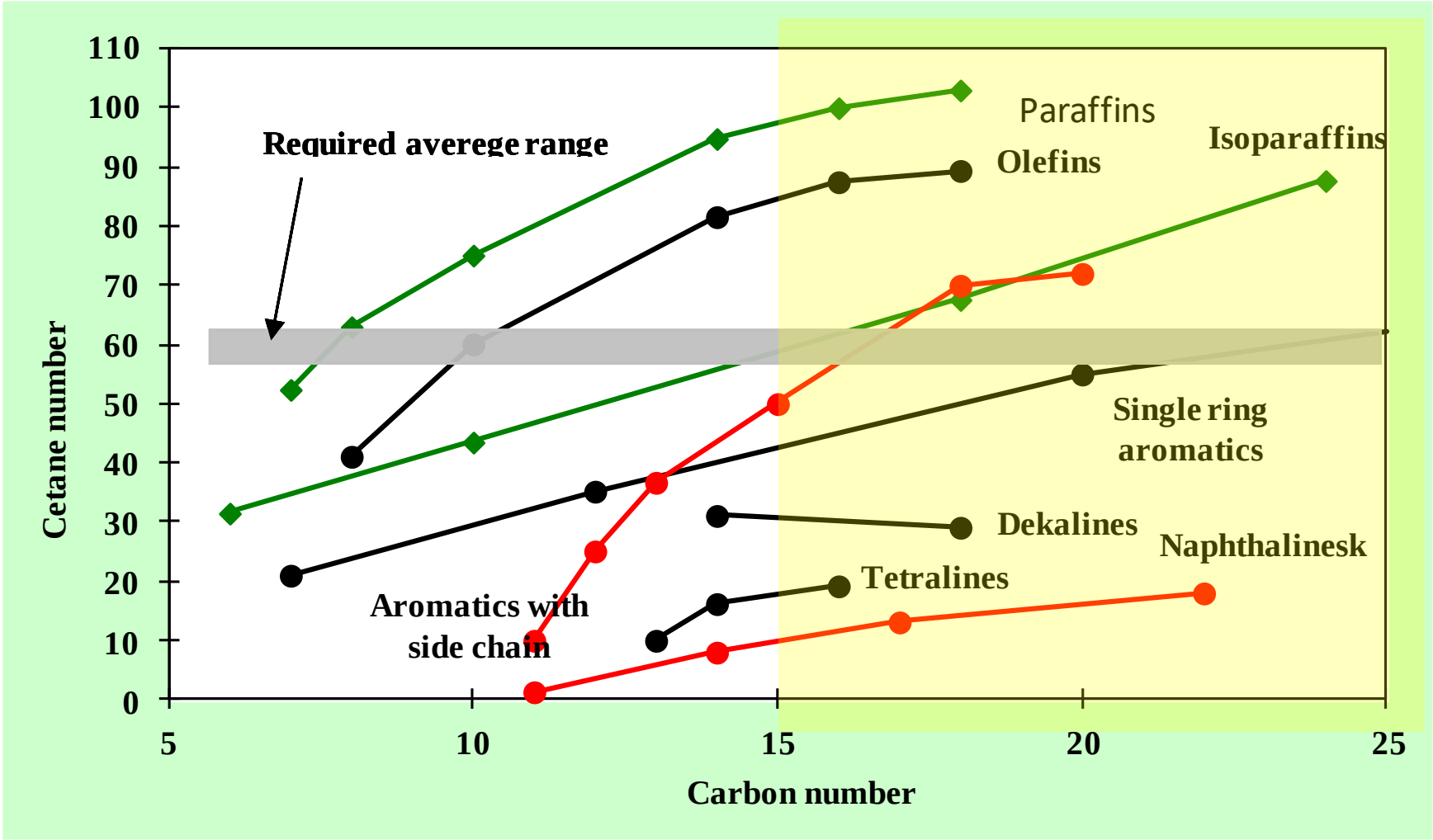
Diesel blending – blending components

Cetane number



Diesel blending – blending components compariso

	Hydrotreated straight run gasoil	JET	Desulphurised gasoil	Biodiesel (FAME)
Specific gravity, (15 °C), g/cm^3	0,880	0,800	0,840	0,883
IBP, °C	175	170	190	320
FBP, °C	365	230	368	360
Cetane number	35	46	53	50
CFPP, °C	-7	-46	-9	-12
Flash point (PM), °C	71	60	80	141
Sulphur content, mg/kg	50	0	2	6
Multiple ring aromatics, m/m%	8	0.1	3	0

Diesel blending – FAME

'... the term biodiesel requires some explanation...'

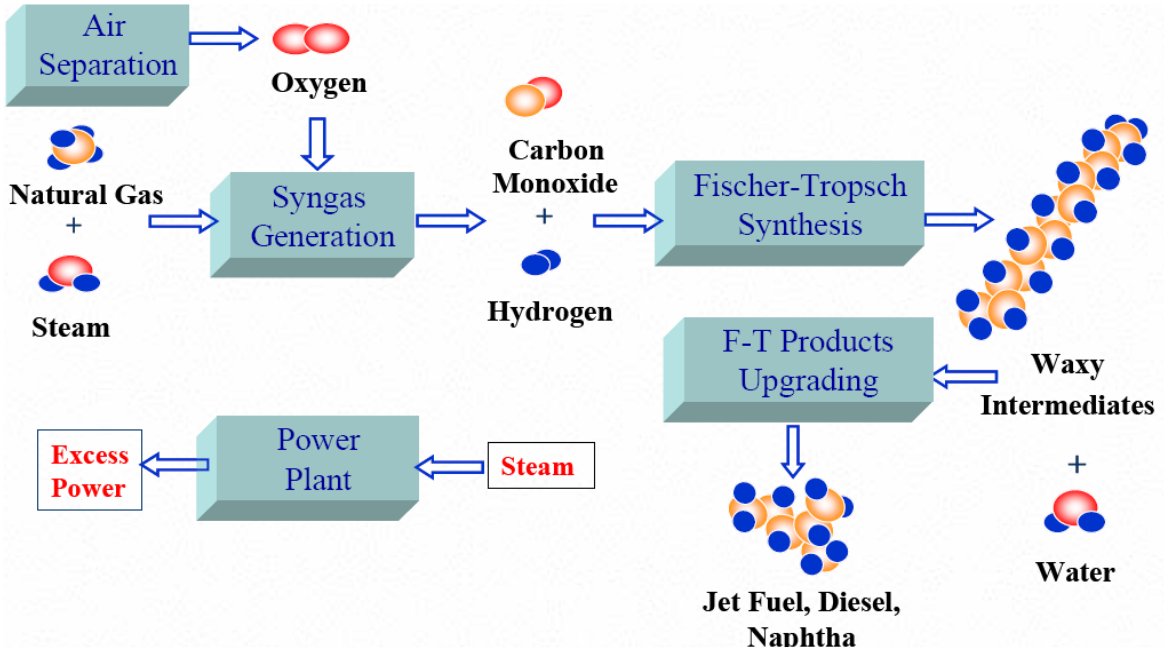
Definition of Biodiesel

- The term Biodiesel is not protected
- The widest definition is:
  Biodiesel is a diesel fuel produced from biomass
- Presently there are 4 types of biodiesel fuels
  1. Pure vegetable oil used as diesel fuel
  2. Transesterified oils and fats: FAME (fatty acid methyl esters)
  3. Paraffines produced from (vegetable) oils and fats: NExBTL
  4. Fisher-Tropsch diesel (green diesel) from gasified biomass
- FAME mixtures are the subject of this work shop and for the ease of speak called Biodiesel

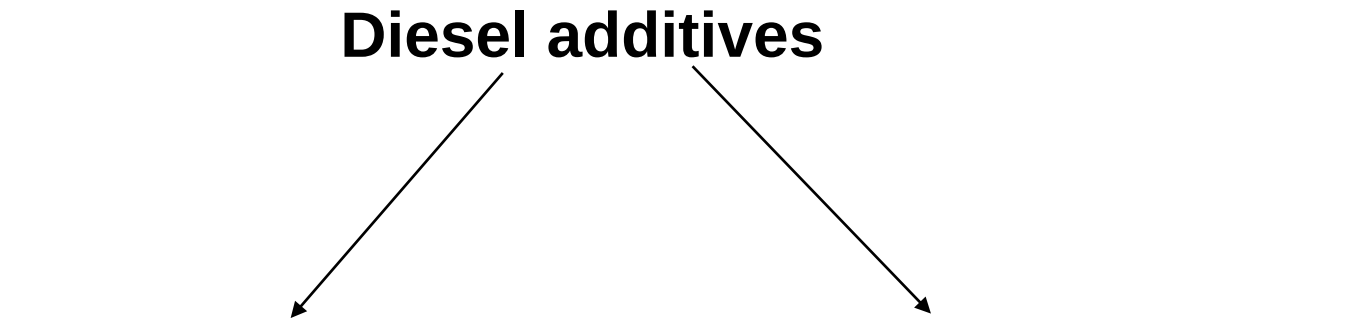
Saybolt
A CORE LABORATORIES COMPANY

„GTL diesel” – a special component

- GTL („gas-to-liquid”) diesel: synthetic diesel, produced by Fischer-Tropsch technology
- Feedstock: natural gas(GTL), coal (CTL), biomass (BTL), wastes
- Quality parameters: high cetane number, low nitrogen, sulphur, olefin and aromatic content



Diesel blending – additives



Refinery additives

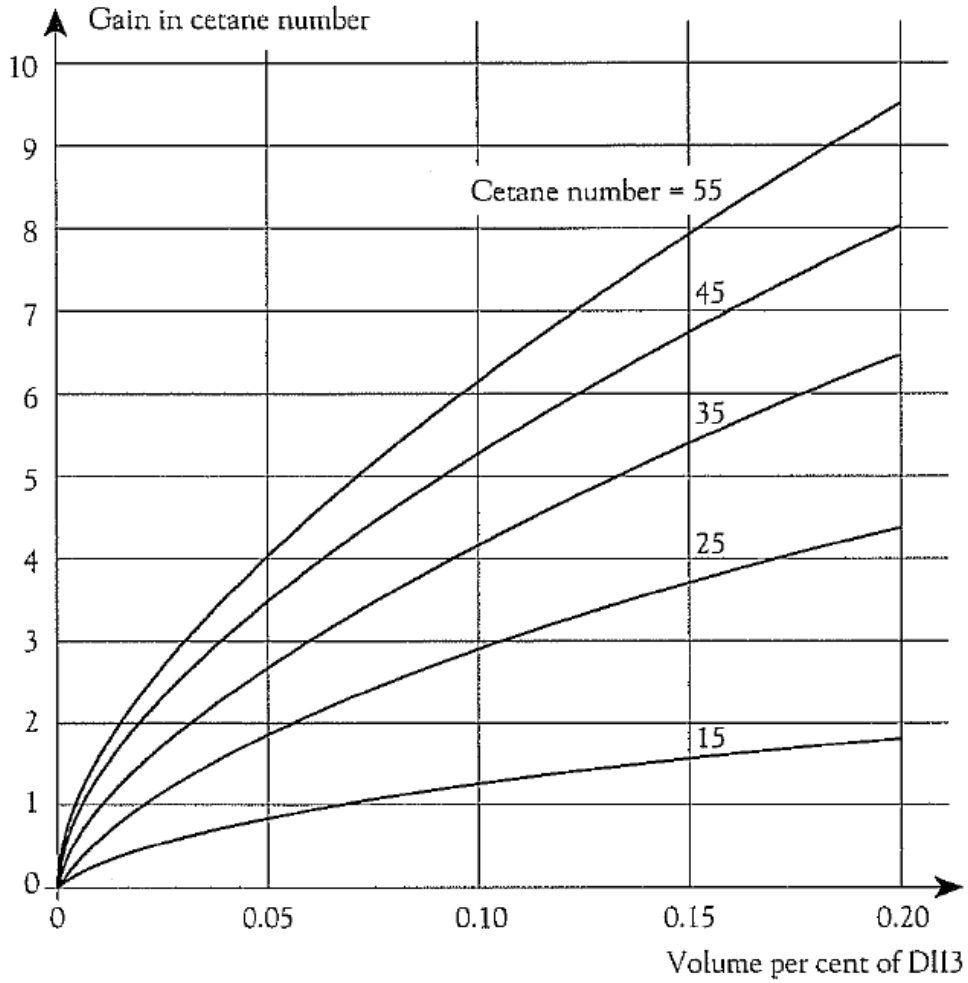
- Cetane improver
- Cold flow improver
- Conductivity improver
- Lubricity improver
- Biocide

Performance additives

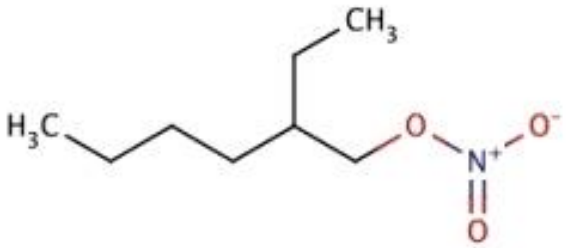
- Performance package
  - Detergents/dispergent
  - Corrosion inhibitor
  - Foam inhibitor
  - Antioxidant

Diesel blending – Refinery additives

Cetane improver



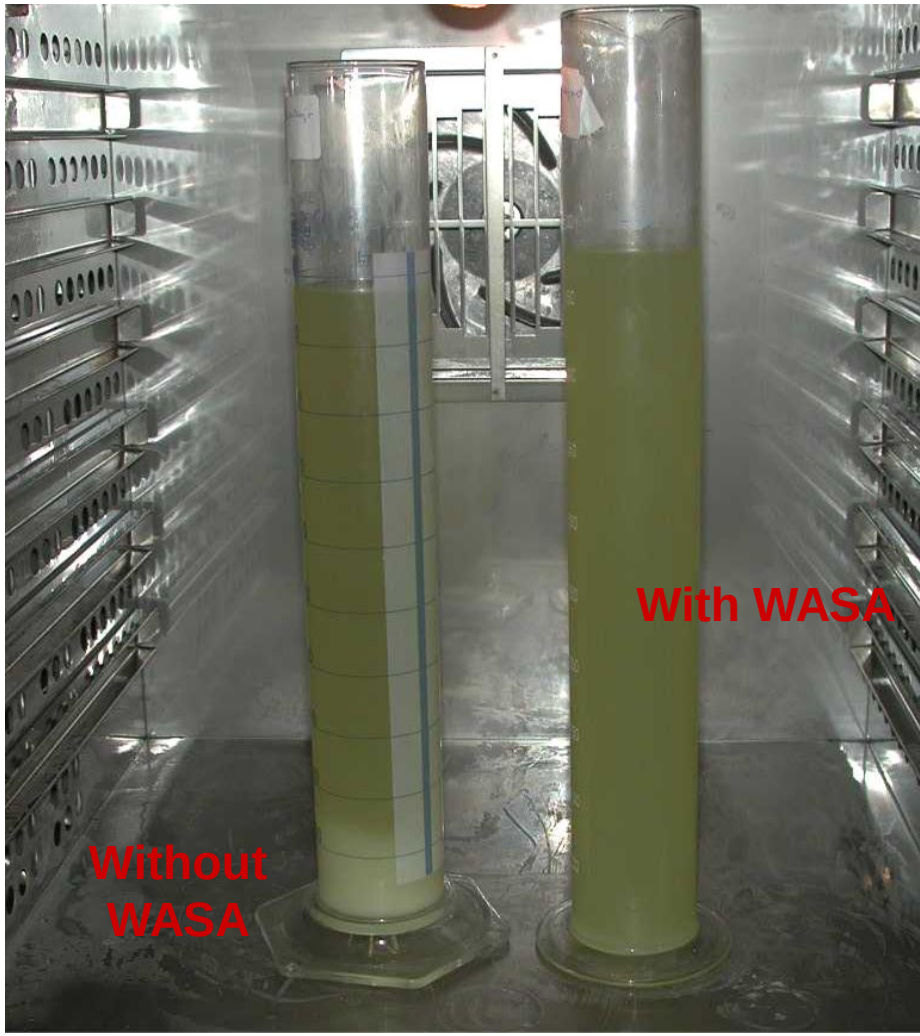
- **Most widely used:**



Diesel blending – Refinery additives

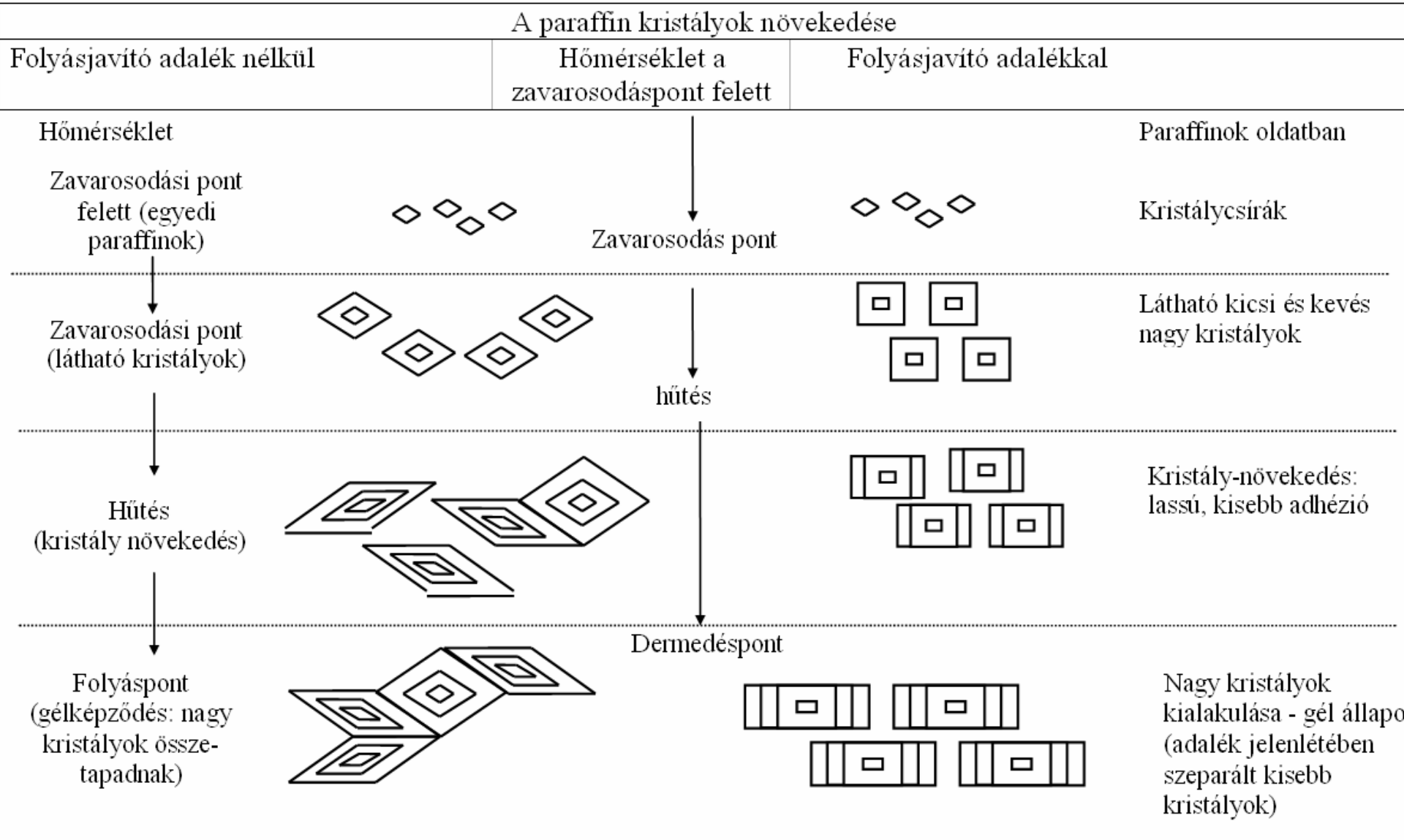
Cold flow improver

- Below the cloud point, the paraffins present in the diesel, starts to crystallize
- MDFI (Middle Distillate Flow Improver) – helps to produce needle shape crystals (one dimensional), instead of table like (two dimensional) crystals (more common way). In this form, the crystals may get across the diesel filter
- WASA (Wax Anti-Settling Additive) – this will help to prevent to settle out the crystallised paraffin



Diesel blending – Refinery additives

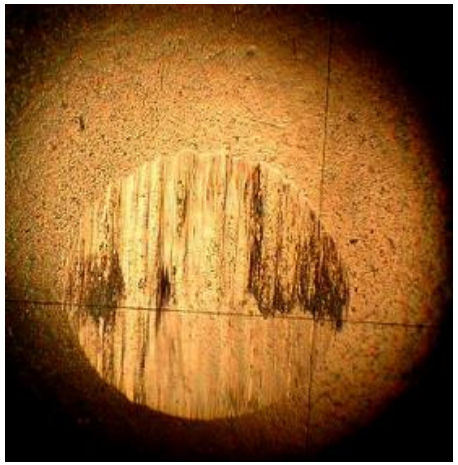
Mechanism of MDFI additive



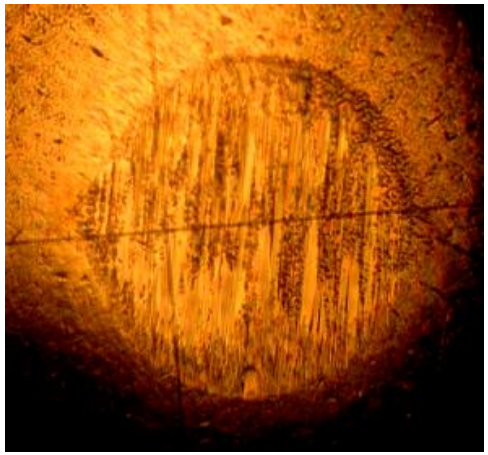
Diesel blending – Refinery additives

Lubricity improver

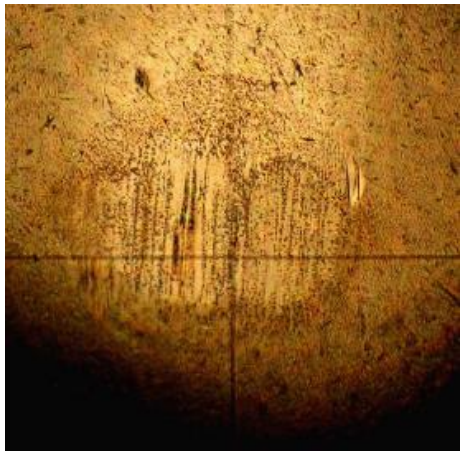
No lubrication

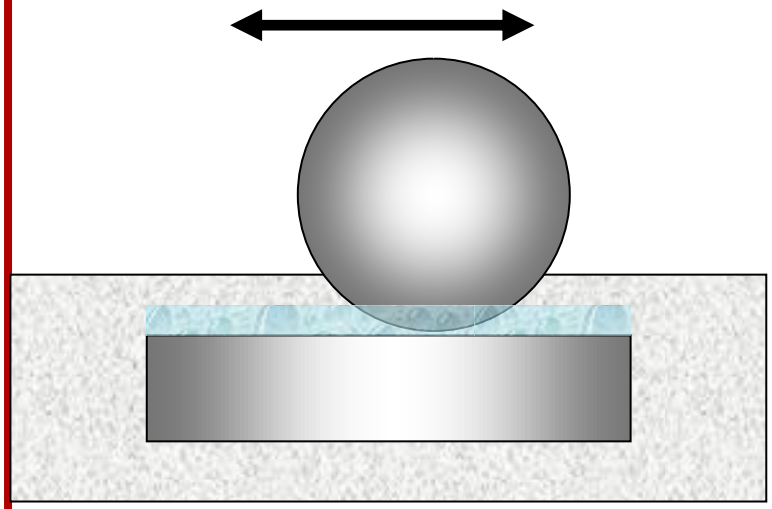


Lubrication just started



Partial lubrication





Full lubrication

Performance additives

Main goal is to prevent damages, increase life time, reduction of consumption, higher power, reduction of emission.

- ✓ Prevention of wear
- ✓ Protection against corrosion
- ✓ Protection against oxidation
- ✓ Improve life time

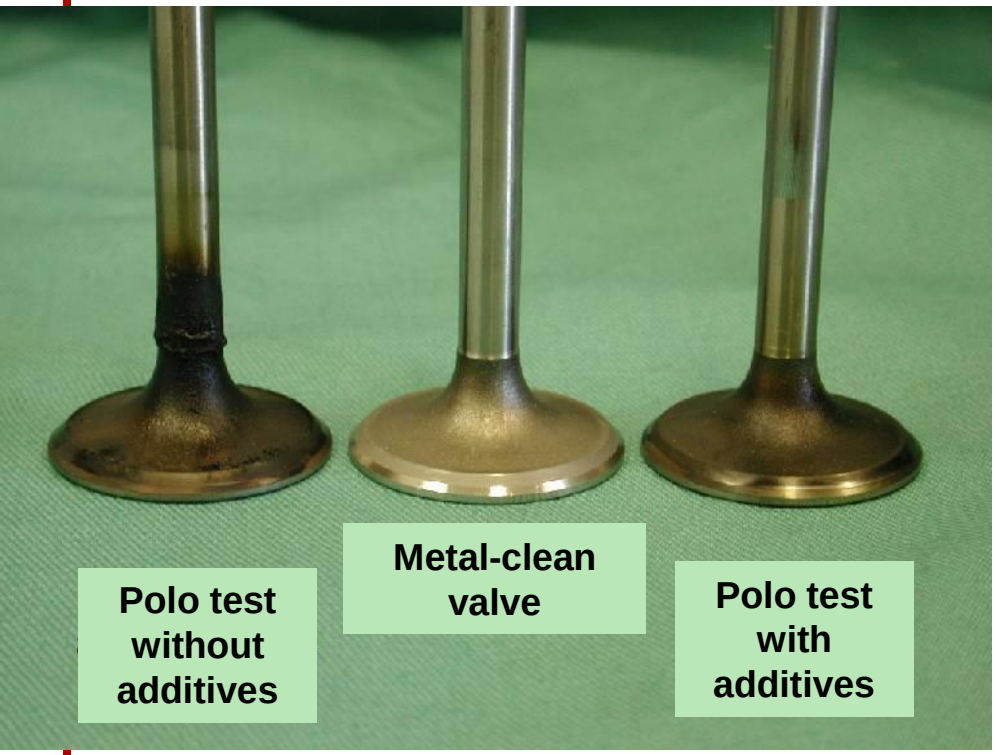
- ✓ Cleanses and keeps clean the fuel supply system
- ✓ Keeps clean the surfaces
- ✓ Reduces consumption

Performance additives

Detergents- dispergents additives

Diesel

Gasoline

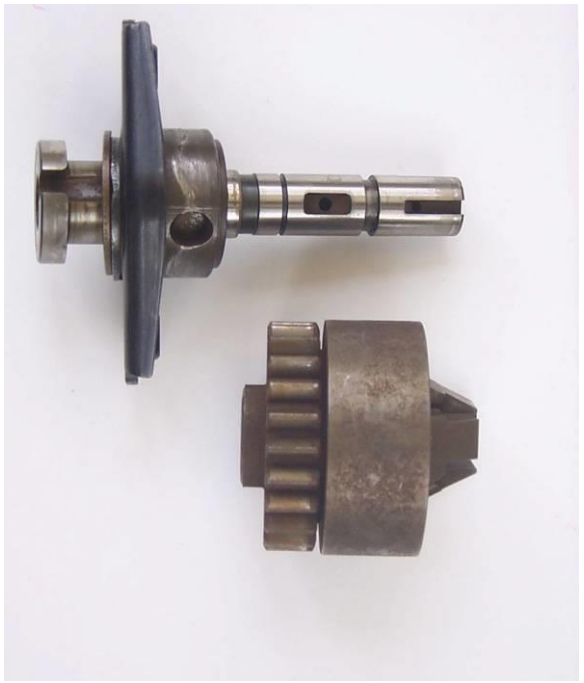


Performance additives

Anticorrosion additives

Refinery samples without additive

MOL TEMPO



diesel fuel pump and injector

**Damages prevention,
longer life!**

Diesel blending – additives I.

Additive	Performance criteria	Type of compound	Proposed concentrations mg/kg
Cetane improvers	Improvement of cetane number, increase of ignition ability (easier cold starting, lower emission, noise, consumption, longer engine life)	2-etil-hexil-nitrát, organic peroxides	100-300
Cold flow improvers	Delivery of good cold flow properties	Mono- and dikarboxylates of polimetacrilates, poliacrilates, alpha-olefin copolimers	150-500
Paraffin dispergents	Inhibition of paraffins settling-out	acryl-aryl-amides,	100-200
Static charge inhibitors	Increased conductivity	Ammonium salts, metal-naphthenates	2-10
Lubricity improvers	Improved lubricity in case of low sulphur diesel (at fuel pump)	Mixtures of unsaturated carboxylic acids	25-100
Biocides	Inhibition of bacteria growth	N,N'-methylene-bis-5-methyloxaazolidine	1-10

Diesel blending – additives II.

Additive	Performance criteria	Type of compound	Proposed concentrations mg/kg
Detergents-dispergents	Inhibition of deposition formation in the fuel system,	Amines, imidazoles, polialkylene-succinimides	30-300
Oxydation inhibitors	Improvement of storage stabity, inhibition of resin formation	Aromatic diamines, 4-methyl-2,6-di-tertier-butyl-phenol	5-30
Metal deactivators	Inhibition of metals, acting as oxydation catalyst (copper), improvement of storage stabity	N,N'-disalyciliden-1,2-propane-diamine	5-20
Demulgeators	Inhibition of clodyness caused by traces of water or other unsolvable materials	Alkyl, dialkyl -sulphosuccinates	10-20
Freeze point reducers	Reduction of freezing point	Ethylen-vinyl-acetate copolimers	75-350
Burning improvers (smoke reducers)	Reduced emission	Iron-carbonyls, lactons, ethers, esthers, dimethoxy-methane	10-30

Diesel blending – additives III.

Additive	Performance criteria	Type of compound	Proposed concentrations mg/kg
Corrosion inhibitors	Inhibition of corrosion of fuel system	Dimer acids, amine salts	10-20
Foaming inhibitors	Inhibition of foaming during tank filling	Poli-methyl-siloxane, silicium-polyether copolimers	1-5
Iceing inhibitors	Inhibition of formation of ice crystals	Glycol-ethers	2-10
Burning-off improvers	Improvement of coke deposition burning on fuel filter, reduction of ignition temperature	ferrocene	5-20
Smell reducers	Neutralisation of unpleasant odours		5-10
Colorers	Quality differentiation	Azo-compounds	5-10

Agenda

- Refinery products
- Motor gasolines
  - Blending components
  - Additives
- Diesel gasoils
  - Blending components
  - Additives
- Blending of motor fuels
  - Blending types
  - Information necessary for blending
  - The blending process
  - Main units of a blending plant

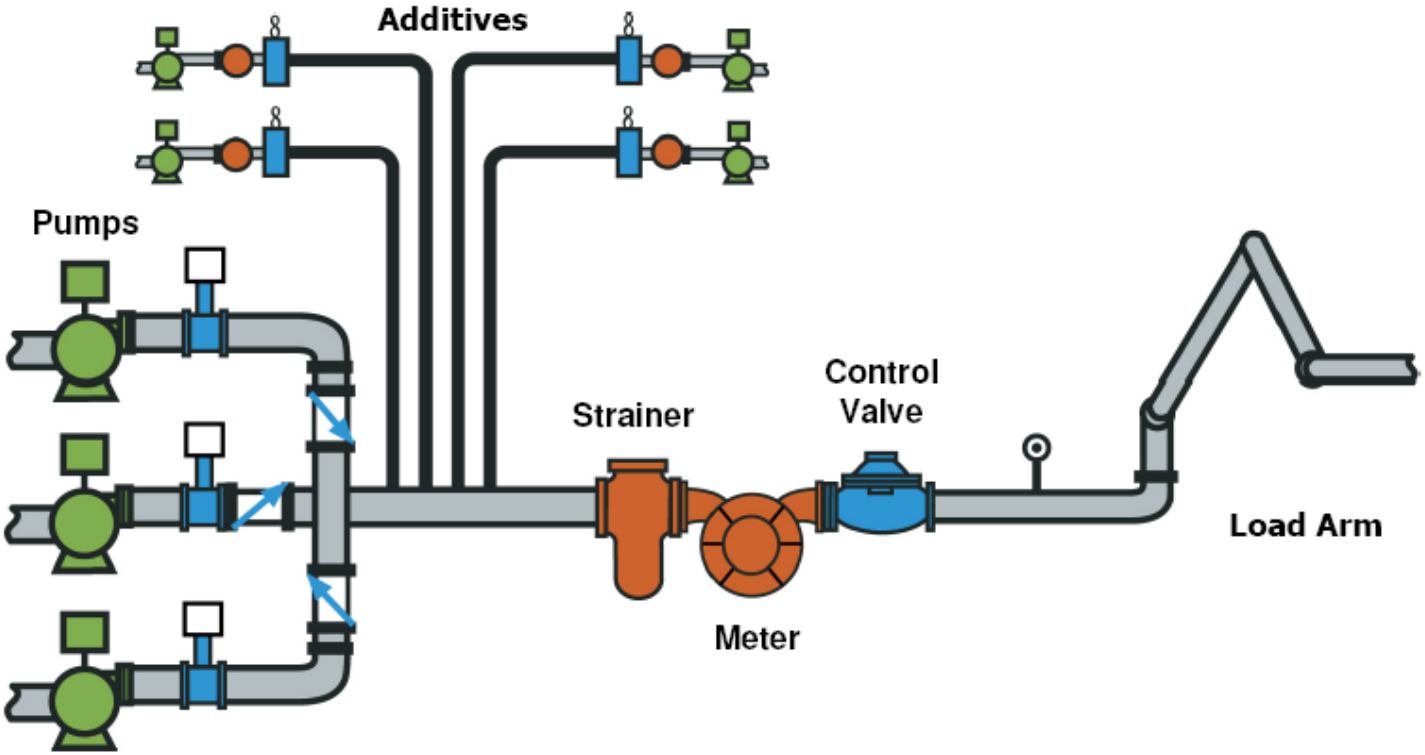
Classification of blending

1. **By sequence of blending**
   - **Sequential blending**
     - **Components charging is done after each other → this needs only 1 flowmeter and controller**
   - **Ratio blending**
     - **Components charging is done paralelly → dedicated flowmeters and controllers needed**

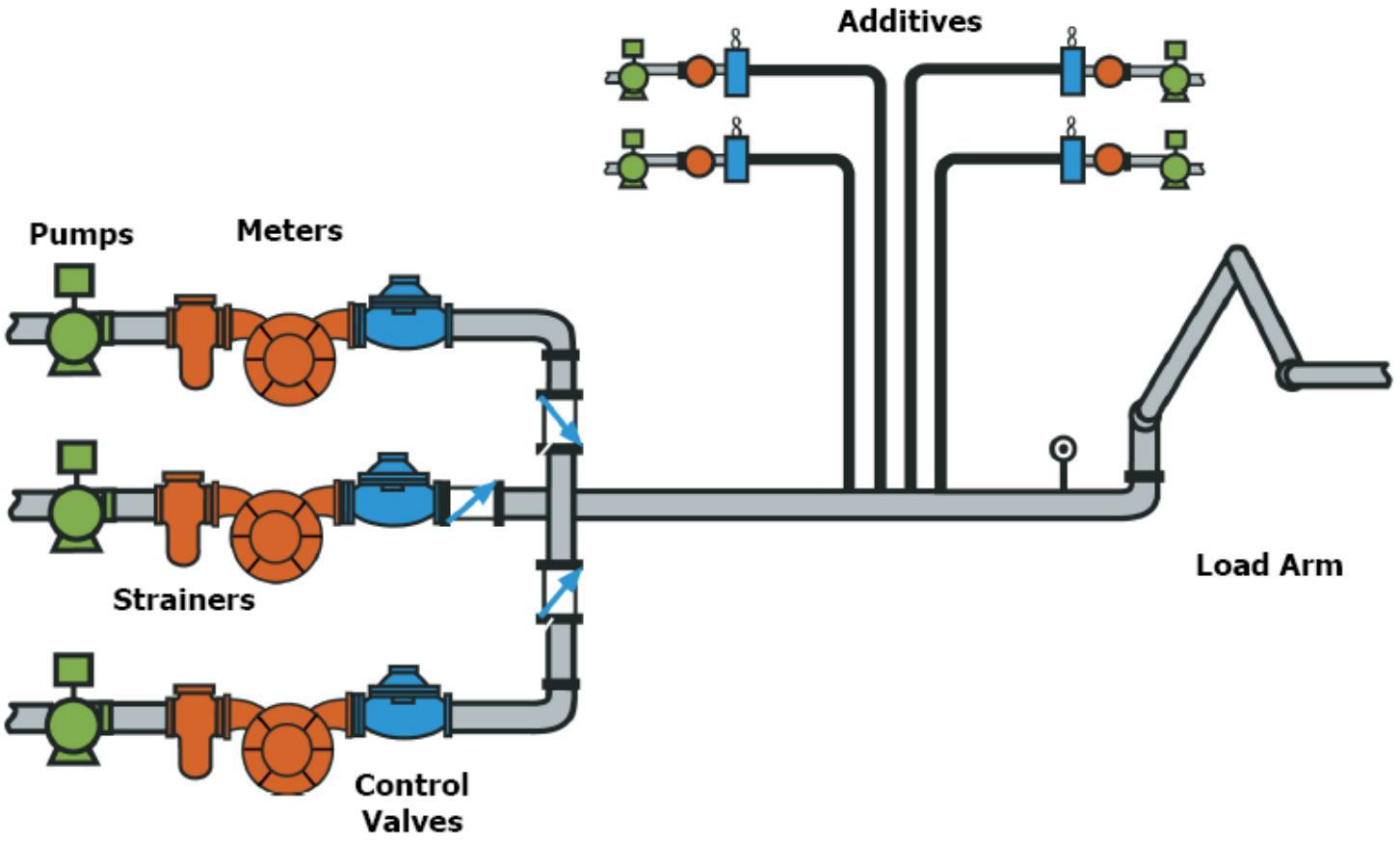
2. **By location of blending**
   - **Batch blending**
     - **Blending is executed from tank to tank**
   - **In-line blending**
     - **Blending is executed from tank to carrier vehicle**

3. **Special types:**
   - **„Wildstream" blending: a third component is produced by blending of two others**
   - **„Sidestream" blending: one special component (e.g. ethanol, additives) are blended to the main component**

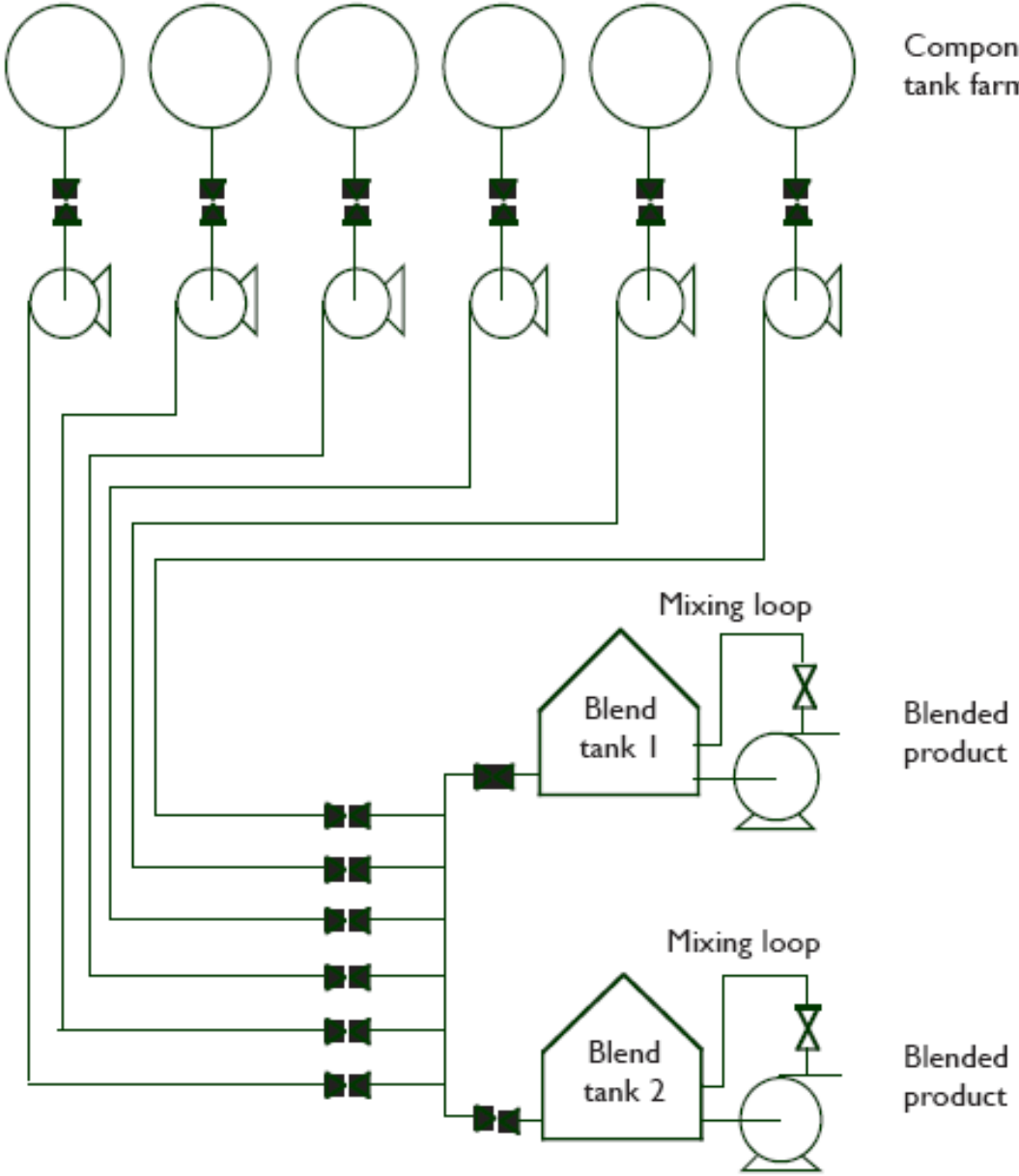
Sequential blending



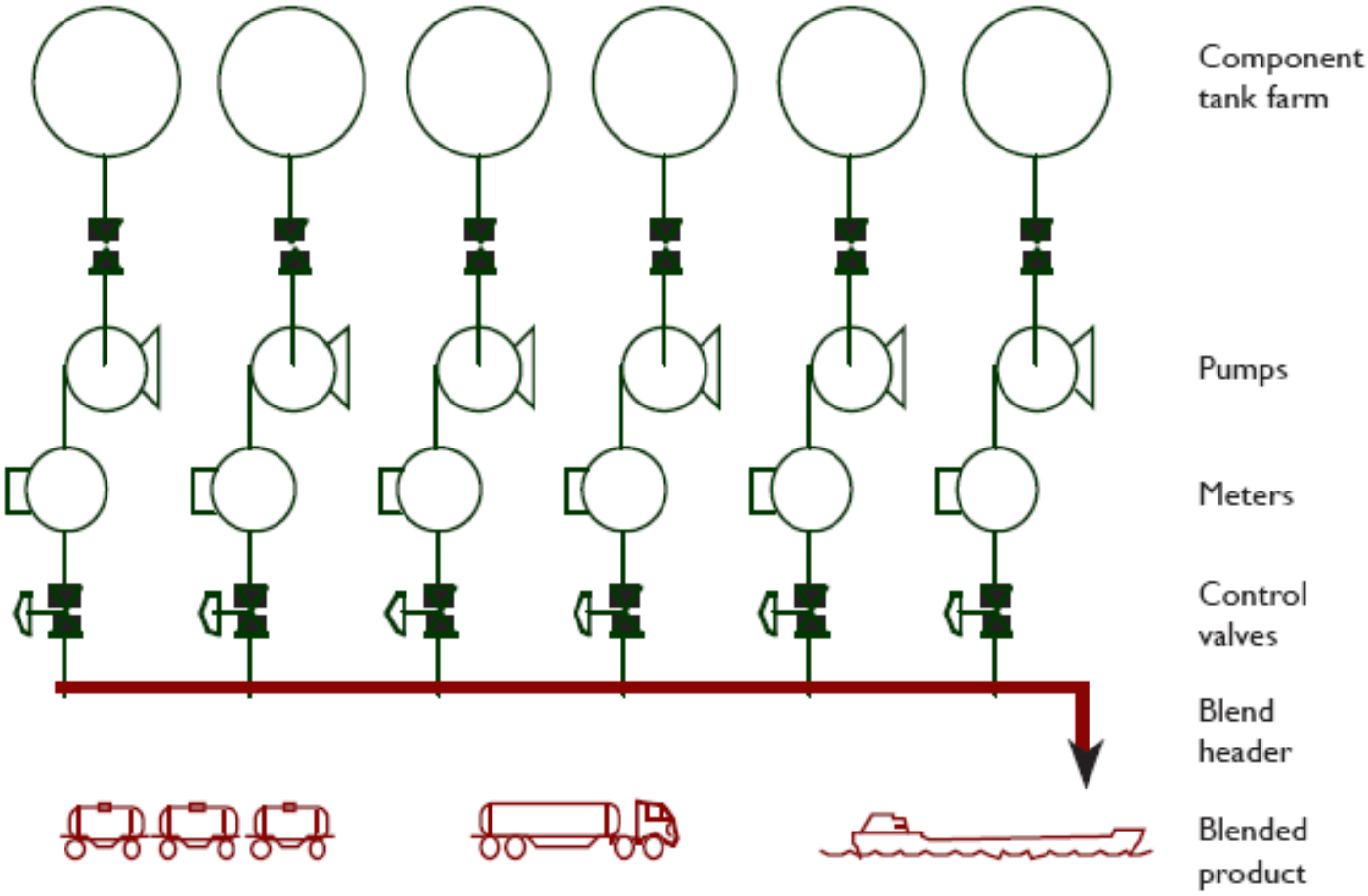
Ratio blending



Batch blending



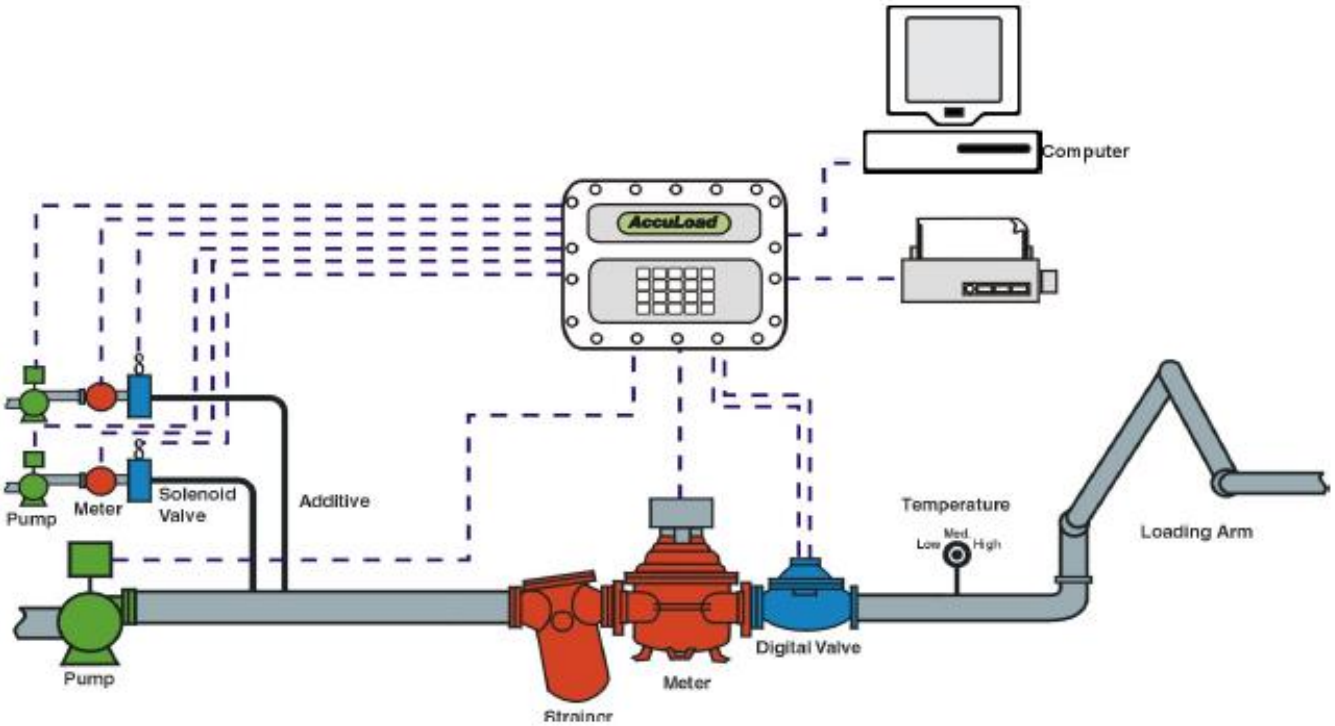
In-line blending



In line blender

Special in-line blending

„Wildstream" or„Sidestream" blending



Comparison of batch and in-line blending

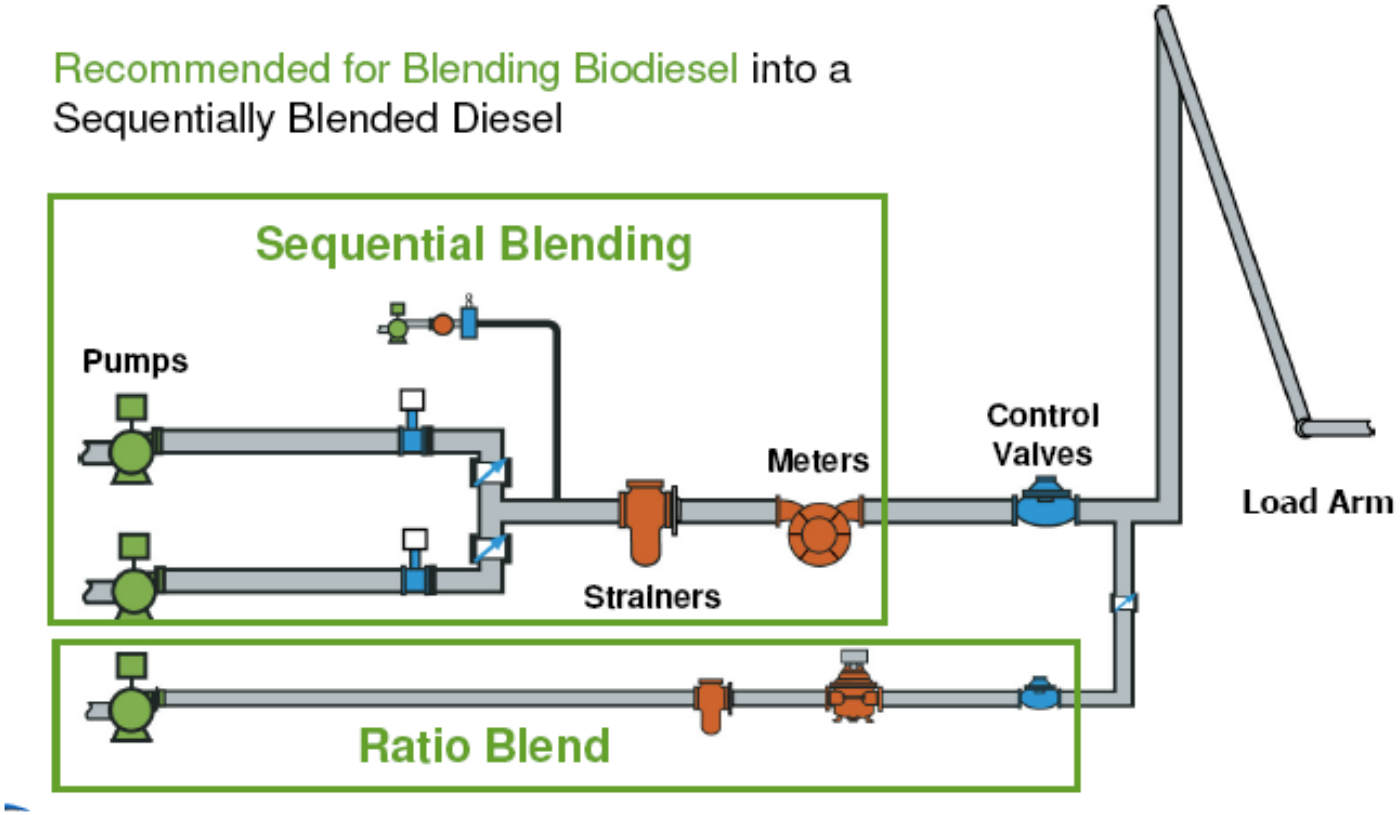
	Batch blending	In-line blending
Blending time	Somewhat longer	short
Tank requirement	For components and products	Only for components
Product tank mixing	necessary	-
Product quality	On-spec at the end of blending only	On-spec of every time of blending
Product availability	at the end of blending only	promptly
Number of products	Defined by number of product tanks	unlimited
Flexibility	low	high

Comparison of batch and in-line blending - example

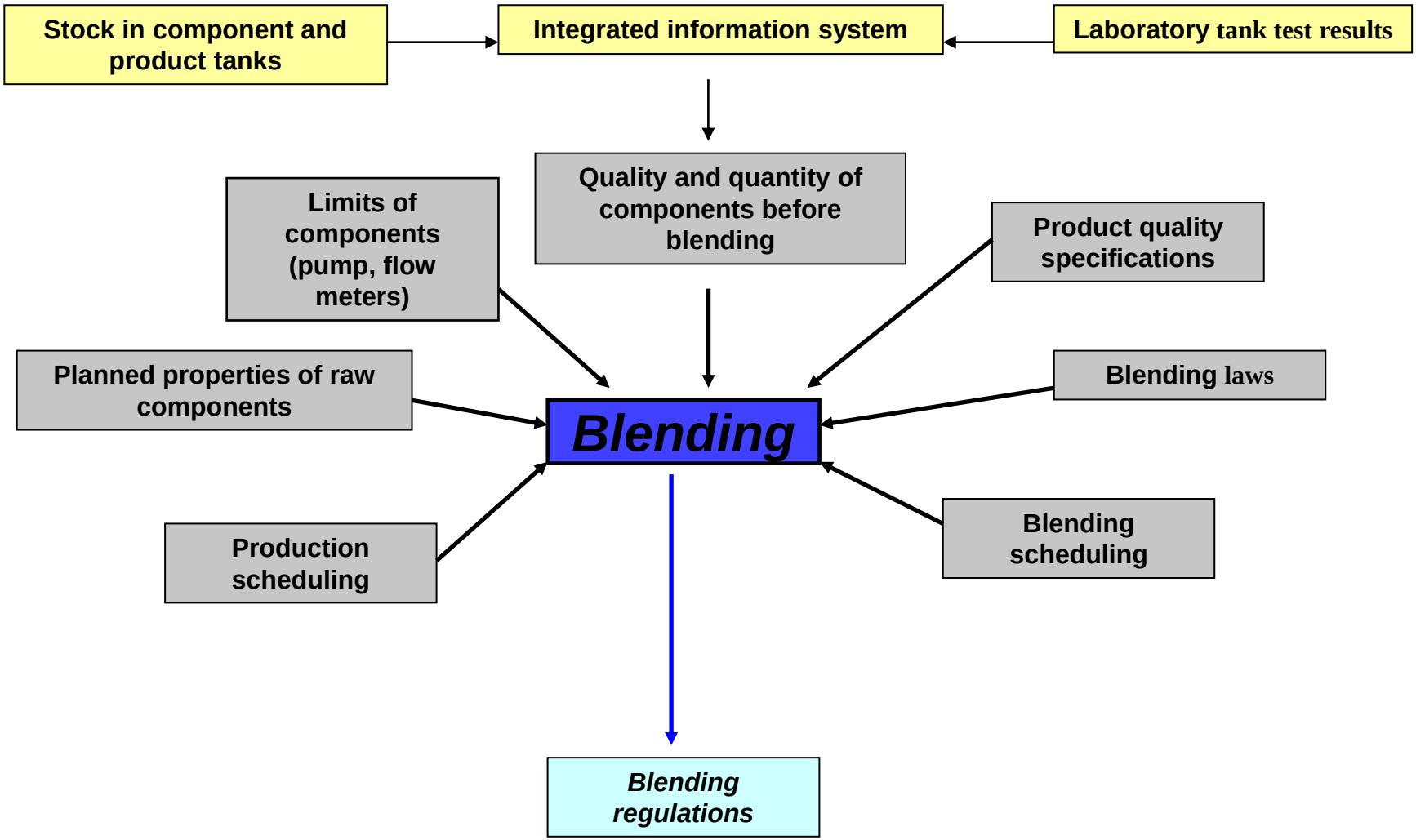
Basis: 100 000 bbl blends both cases; 5000 bbl/hr product pumps both cases

Case 1: In-Line blending	
100 000 bbl pipeline blend @ 5000 bbl/hr =	20 hours
Case 2: Tank blending	
95 000 bbl initial tank blend @ 5000 bbl/hr =	19 hours
Tank testing and analysis	2 hours
Creation of "fix-up" blend based on test results	1 hour
5000 bbl "fix-up" tank blend @ 5000 bbl/hr =	1 hour
	23 hours

Hibrid blending systems



Information needed for blending



Information needed for blending
Quality and quantity of components before blending

- **Available quantity of blending components**
  - **Stock in tank**
  - **+ actual production (in case of „increase-decrease”)**

- **Quality of blending components**
  - **Laboratory test results**
  - **+ actual production quality (in case of „increase-decrease”)**

- **Quantity of product in product tank before blending**
  - **Bottom stock**

- **Quality of product in product tank before blending**
  - **Based on quality certificate**

MOL Magyar Olaj- és Gázipari Nyilvánosan Működő Részvénytársaság

TARTÁLY BATCH MINŐSÍTÉS

MSZ ISO 9001: 2008 / SGS HU 94/4326

Azonosító: QC_1_MOL01/ mol_batch_certificate_a

Bizonylatszám: 232805/1/ 2023912

Termék: Kénmentes dízelgázolaj B7, téli (F)
MOL_0611_001_T

Termékszabvány: MSZ EN 590

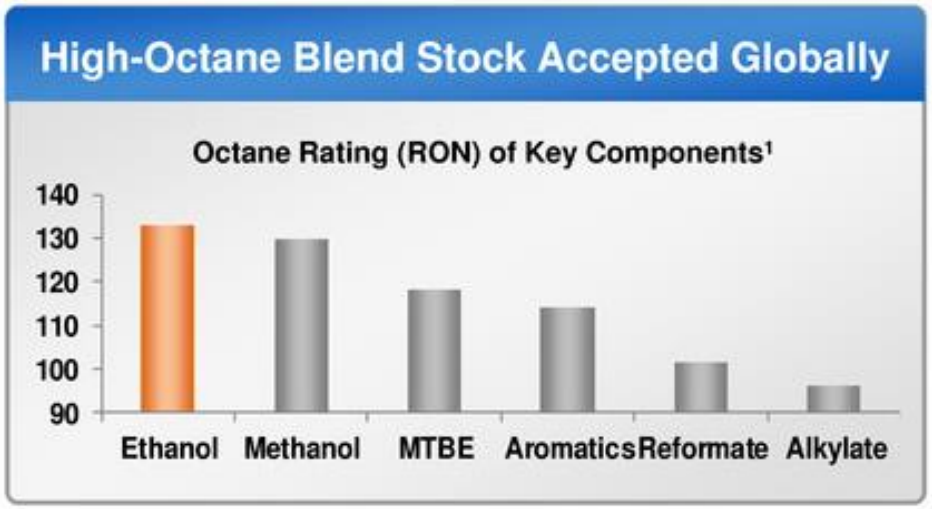
Üzem: DFLTT20038
Tartály / Batch szám: DT20038 / 551
Mintavétel időpontja: 2012.01.01. 06:24
Mintajóváhagyás: 2012.01.01. 09:48
Mintagazda: DP1
DF NÜTM diszpécserek

Réteg	Vizsgálati módszer	Szabvány	Mérési adat	Követelmény

Information needed for blending
Planned properties of raw components

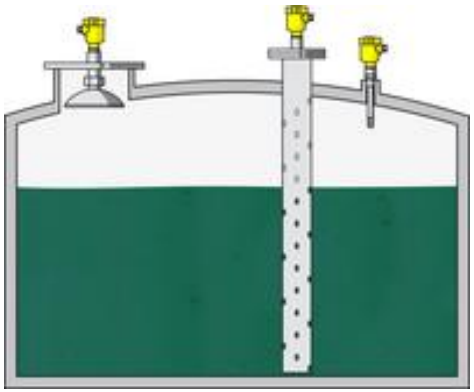
- Quantity
  - Planned
  - Different from planned (shut-down, capacity change…)

- Quality
  - Planned
  - Different from planned
    - Feedctock quality/quantity
    - Capacity change



Information needed for blending
Limits of blending

- Quantity (level) of components and products in tanks
  - Minimum values – blending components
  - Maximum values – product



- Blendable quantity of components
  - Pump capacity (max., min.)
  - Flow meters and controllers operating range

- Maximum number of blendable components
  - Valves, pipe connections…

- Blending schedule
  - E.g. premium product vs. main product

Information needed for blending
Product quality specifications

- **Specifications, standards**

- **Internal specifications (more severe than standards)**

- **Specifications for premium products (individual specifications)**

Information needed for blending
Blending laws

- **Linear correlations**
  - **Specific gravity, S-, benzene-, aromatic-content...**
- **Non-linear correlations**
  - **May be linearised by bonuses**
    - **RON, MON, distillation properties…**
  - **May be linearised by formulas**
    - **Cetane index, flash point, viscosity…**
- **Impact of additives**

Cetane Blending Index - formula :

CIX is modeled according to ISO4926 as follows:

$$\mathbf{CIX} = 45.2 + 0.0892 \cdot \mathbf{T10} + (0.131 + 0.901 \cdot (e^{-3.5 \cdot (D-0.85)} - 1)) \cdot \mathbf{T50} + (0.0523 - 0.42 \cdot (e^{-3.5 \cdot (D-0.85)} - 1)) \cdot T90 + 0.00049 \cdot (\mathbf{T10}^2 - \mathbf{T90}^2) + 107 \cdot (e^{-3.5 \cdot (D-0.85)} - 1) + 60 \cdot ((e^{-3.5 \cdot (D-0.85)} - 1))^2$$

D = density @ 15 C
T10 = Evaporated up to 10 %
T50 = Evaporated up to 50 %
T90 = Evaporated up to 90 %

Viscosity - formula

Maxwell blending index method [D1] – pages 69, 70 - volumetric blending

$$VBN = 59.58959 - 21.8373 \ln (\ln (CST + 0.8))$$

$$CST = EXP[EXP\{(VBN - 59.58959)/(-21.8373)\}] - 0.8$$

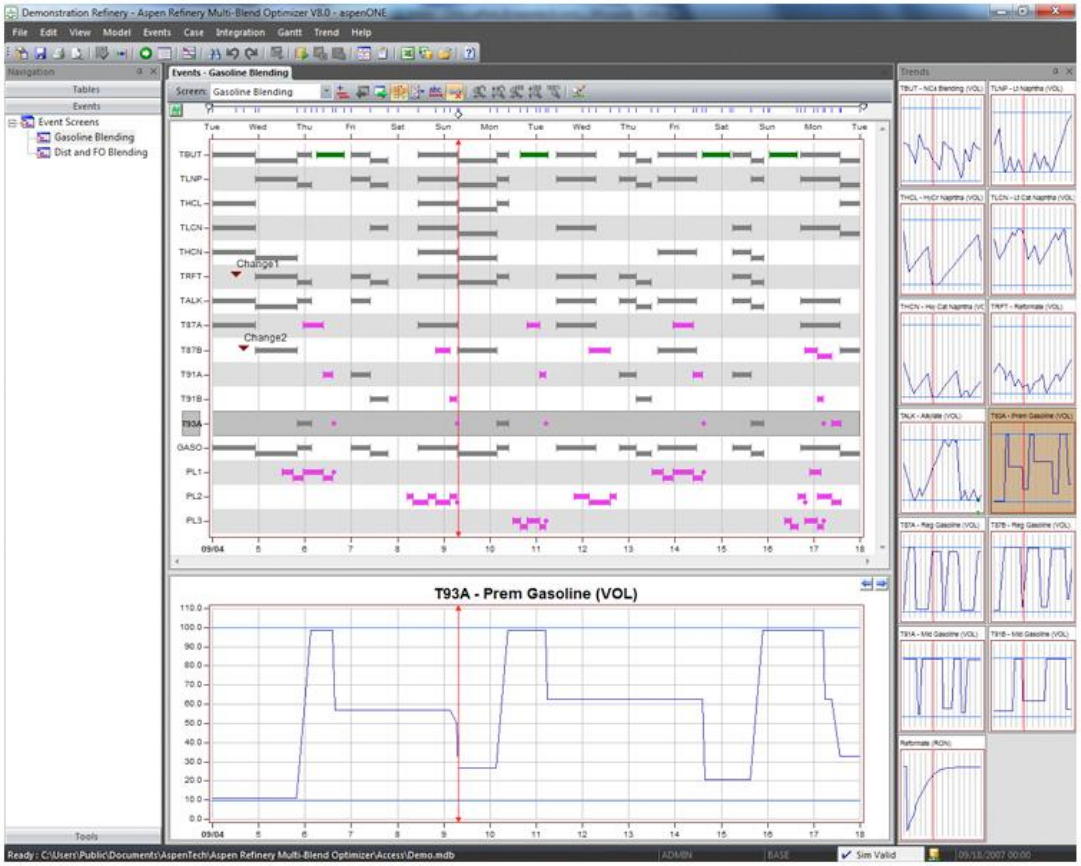
VBN = viscosity blending number

CST = viscosity in centistokes

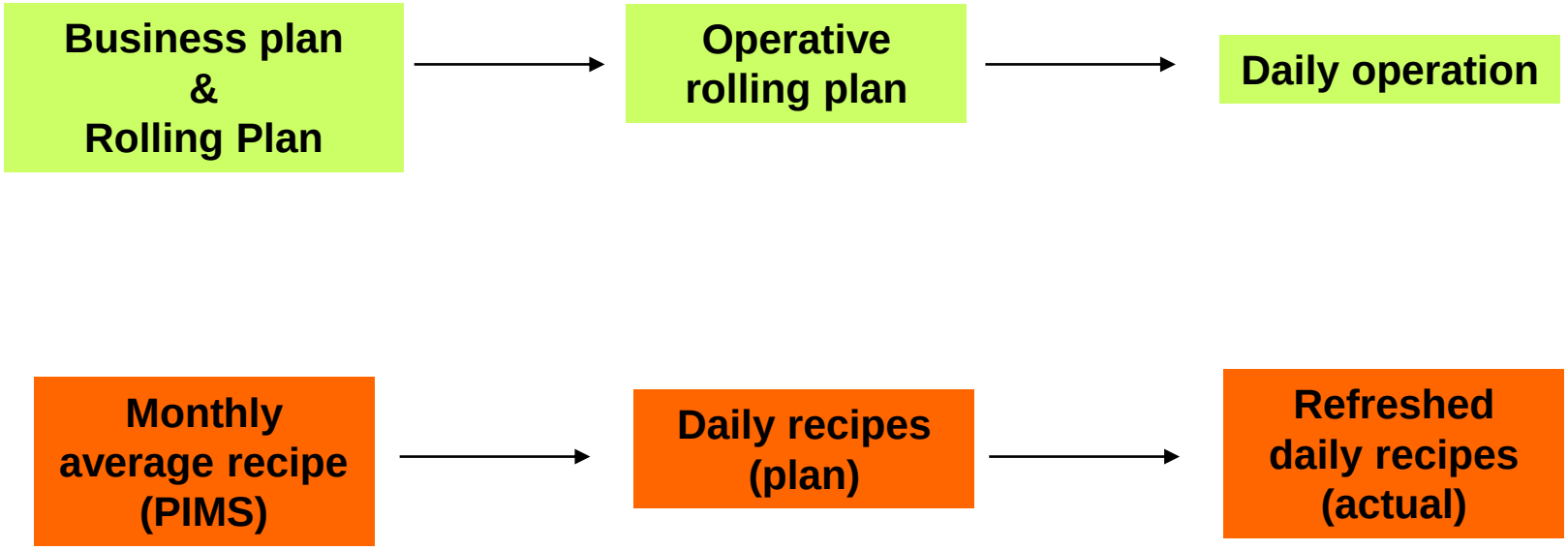
Information needed for blending
Production and blending scheduling

- **Production scheduling**
  - **Opening stocks**
  - **Actual production**

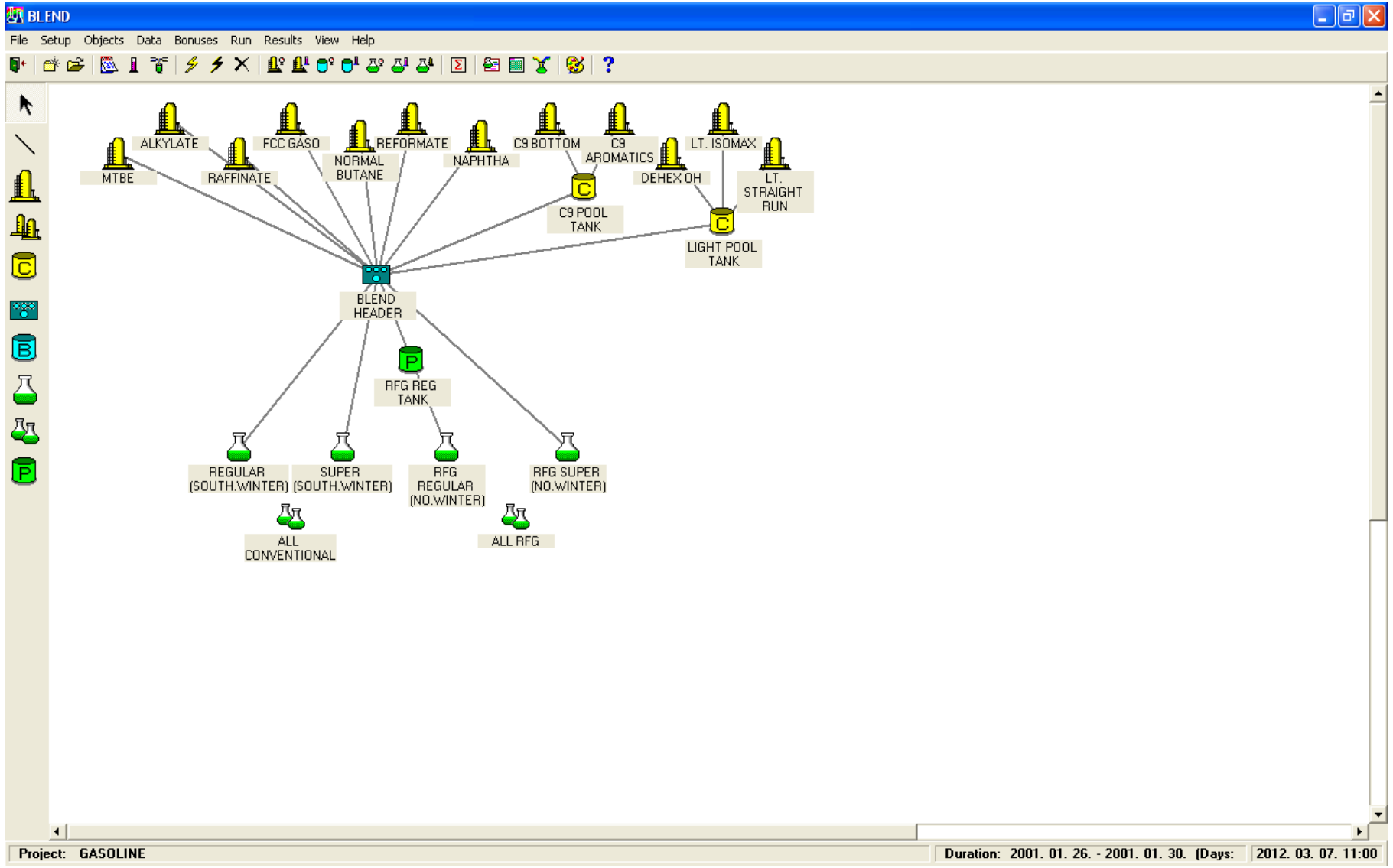
- **Blending scheduling**
  - **Availability of components**
  - **Blender capacity**
  - **Logistics scheduling**



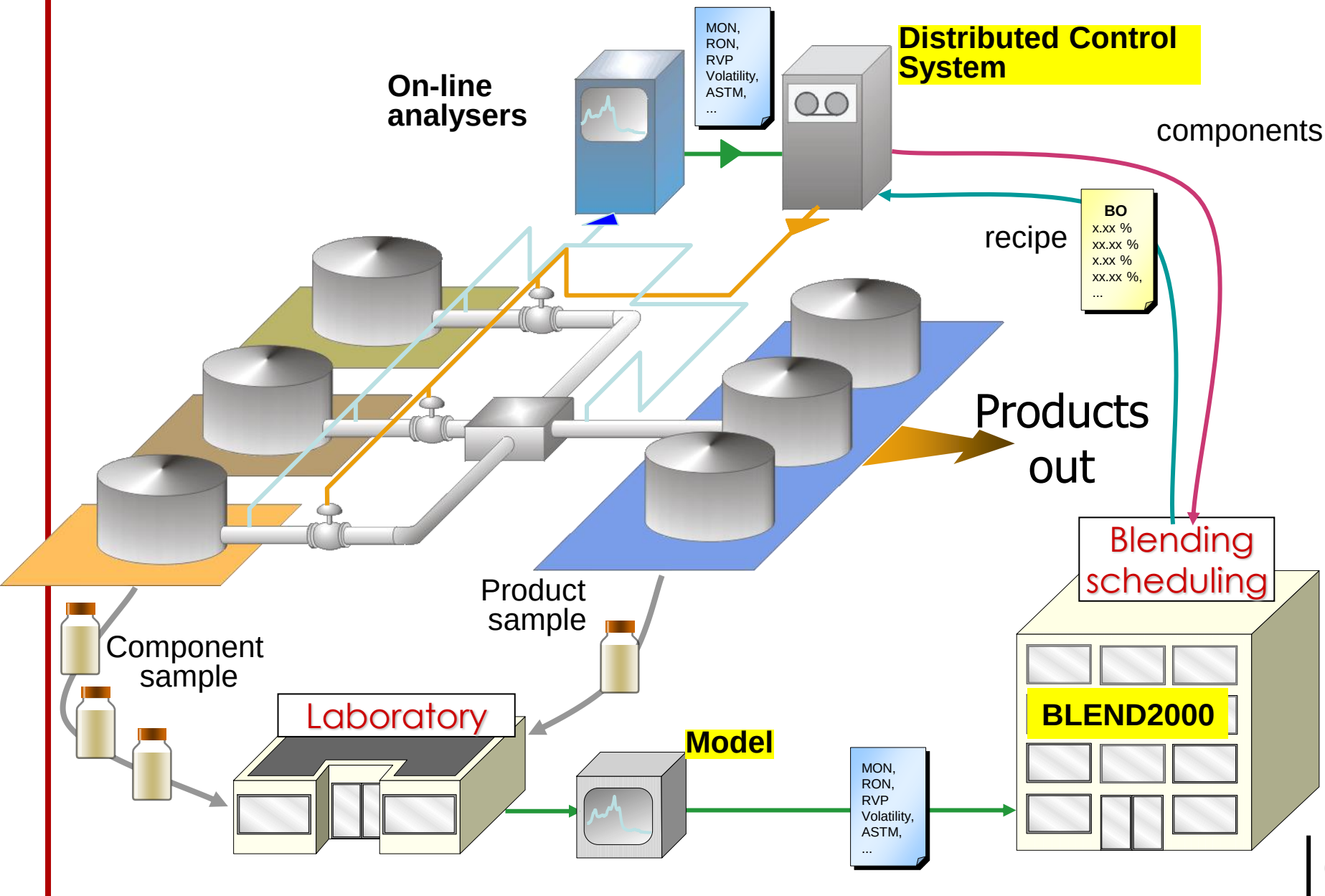
Way of blending
Formation of blending recipes



Blending optimisation



Way of blending

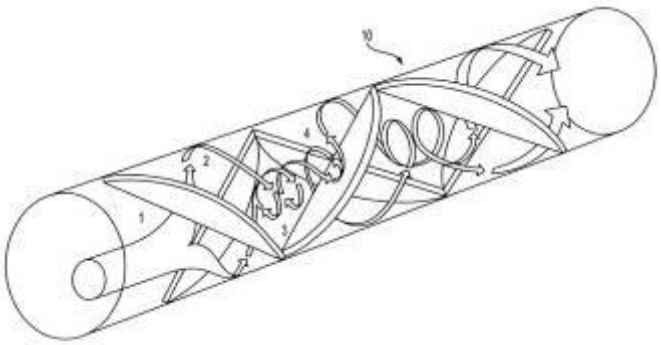


Main parts of the Blender Unit - 1

„Tankfarm”

Main parts of the Blender Unit - 2

Static mixer



Main parts of the Blender Unit - 3

On-line analysers

NIR

Sulphur meter

Density meter

Distillation device

MKrar@MOL.hu