Marine Methanol Fuel Specification and Engine Technologies

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Agenda

Methanol as a Marine Fuel

Methanol Combustion Properties

Methanol Fuel Quality

Methanol Purity from Direct and Indirect Production Pathways

Energy Converters Fuel Requirements and Specifications

Existing Standards and Specifications

Recommendations

Methanol Engine Technology and Development Progress

Overview of ignition strategies

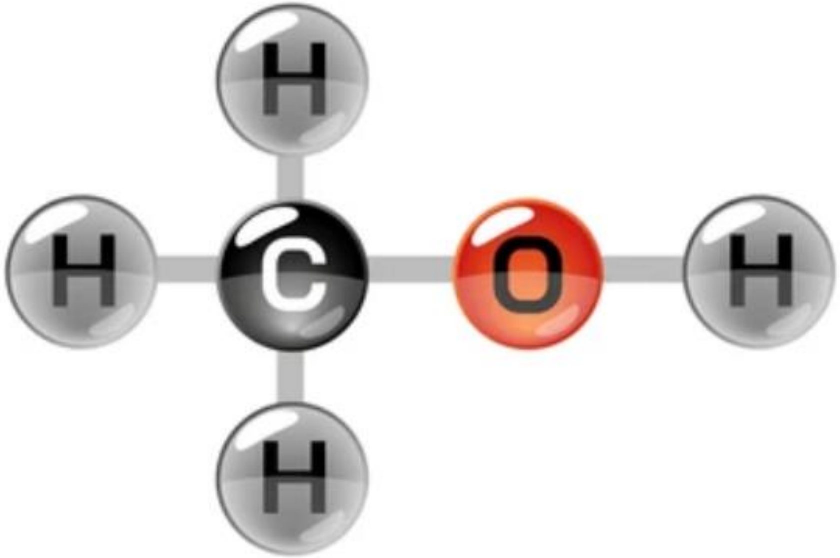
Combustion Concepts for Methanol Diesel (compression-ignition) Engines

Current Development Status

1. Methanol as a Marine Fuel

Methanol Combustion

Properties



1. Methanol as a Marine Fuel

High octane number
- High latent heat of vaporisation ΔH_{vap}
- Low vapour pressure
- High autoignition temp.
- High LFL

Fully miscible with water

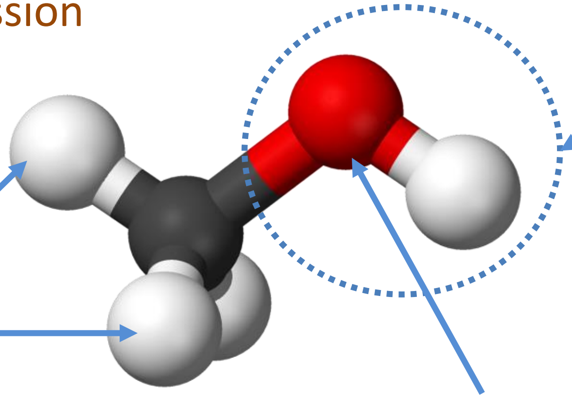
Low cetane number
- Cold start issues
- Ignition issue

Less carbonaceous particulate and deposit

Formaldehyde emission

No C-C bond

Polar –OH group



High H:C

Lower CO_2 emission

<u>CO_2 emission factor ($kgCO_2/L$)</u>

Methanol: 1.08

Gasoline : 2.32

Diesel : 2.71

Oxygenated

Reduce incomplete combustion and CO emission

Reduce excess air, lower AFR, greater combustion efficiency

Higher burning velocity

Lower energy density, long injection duration

Combustion Reaction

Methanol: $CH_3OH + 1.5O_2 \rightarrow 1CO_2 + 2H_2O$

Methane : $CH_4 + 2O_2 \rightarrow 1CO_2 + 2H_2O$

Propane : $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

Butane : $C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$

Molar expansion ratio (MER) > 1

1. Methanol as a Marine Fuel

Fuel management-related properties

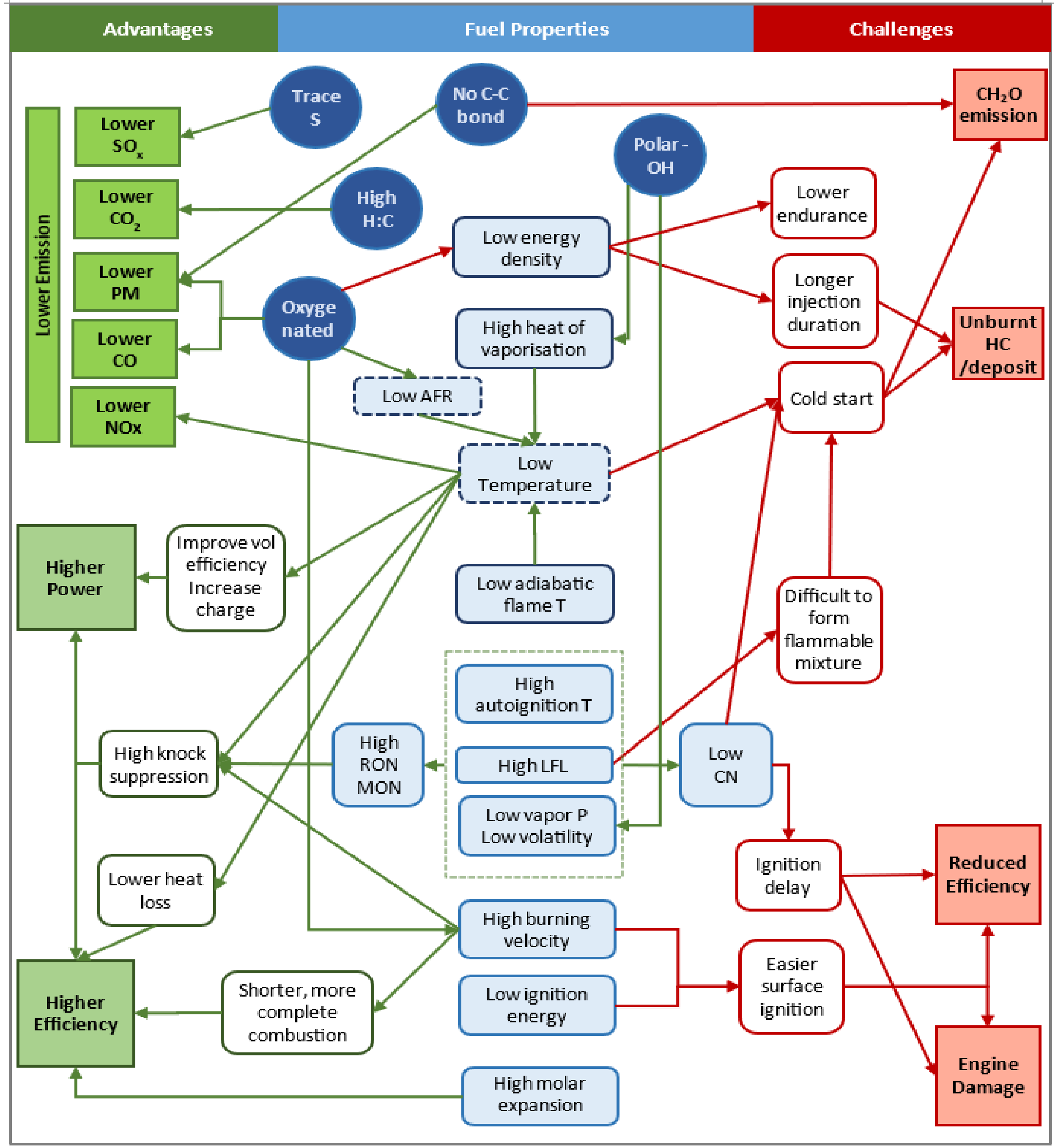
Liquid fuel at ambient temperature

Low density, viscosity, surface tension
Easy to atomise, no pre-heating required, no cold-flow issue

Low lubricity
Accelerate engine wear and tear

Low flash point, wide flammability range
Safety issues

Corrosive
Corrosion issues, particularly with presence of water



2. Methanol Fuel Quality

Methanol Purity from Direct and Indirect Production Pathways

Energy Converters Fuel Requirements (Marine Engines & Fuel Cells)

Chemical and Industrial Standards

Standards for Motor vehicles

Standards for Marine Application

Recommendations

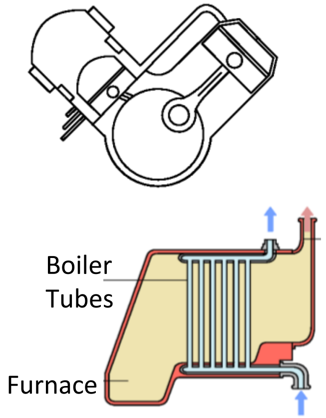
2. Methanol Fuel Quality

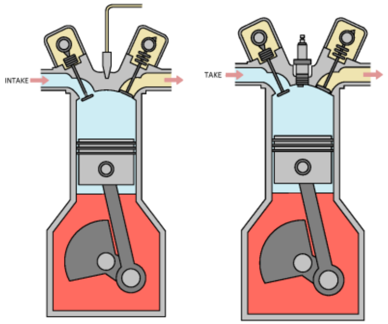
Energy Converters Requirements

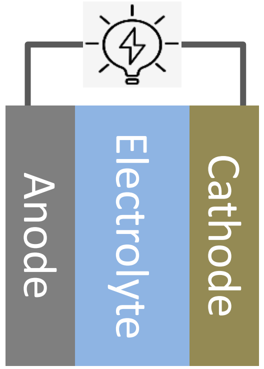
External Combustion
Boiler
Gas Turbine
Steam Engine
Stirling Engine

Internal Combustion
Spark Ignition (Gas Engine)
Combustion Ignition (Diesel Engine)

Fuel Cells
PEM
SOFC
DMFC







Methanol Fuel Purity

Feedstock → Synthesis Processes → Storage Transportation

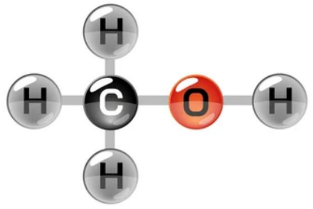
Intrinsic (impurities)
- Composition
- Reaction by-products

External (contaminants)
- Contamination during extraction
- Catalytic fines
- Solvent / Sorbent / Oxidant
- Sea water contamination
- Air ingress / Material degradation

Existing Specifications & Standards

- Chemical Grade
- Industrial Grade
- Motor Vehicle
- Fuel Cell
- Conventional Marine Fuel
- Methanol Engine Manufacturer Specifications
- Hydrogen for Fuel Cells

2. Methanol Fuel Quality
- Feedstock and Production Pathways



Feedstock

- H_2 (water)
- CO_2 (air)
- CO_2 (flue gas)
- CO_2 (other process)
- Natural gas
- Coal
- Biomass
- Biogas

Direct Pathway

CO_2, H_2 Generation
- Carbon capture
- Electrolysis of water

Methanol Synthesis
- Direct hydrogenation of CO_2 with H_2

Purification
- Distillation, Stripping etc.

Indirect Pathway

Syngas production
- Gas Reforming
- Carbonaceous solid Gasification

Methanol Synthesis
- Syngas cleaning & conditioning
- Methanol synthesis

Purification
- Distillation, Stripping etc.

Direct Pathway			
Methanol Forming	:	$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$	$\Delta H = -49\ kJmol^{-1}$
Water-Gas-Shift	:	$CO_2 + H_2 \rightleftharpoons CO + H_2O$	$\Delta H = -41\ kJmol^{-1}$

Indirect Pathway			
Methanol Forming	:	$CO + 2H_2 \rightleftharpoons CH_3OH$	$\Delta H = -91\ kJmol^{-1}$
	:	$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$	$\Delta H = -49\ kJmol^{-1}$
Water-Gas-Shift	:	$CO_2 + H_2 \rightleftharpoons CO + H_2O$	$\Delta H = -41\ kJmol^{-1}$
	:	$CO + H_2O \rightleftharpoons CO_2 + H_2$	$\Delta H = +41\ kJmol^{-1}$

2. Methanol Fuel Quality
- Biomass Feedstock

Organic

- Cellulose
- Hemicellulose
- Lignin
- Proteins
- Lipids
- Simple sugar
- Starch
- Chlorophyll
- Waxes

Inorganic

Macronutrients

Nitrogen
Phosphorous
Potassium
Calcium
Magnesium
Sulphur

Micronutrients

Chlorine
Boron
Iron
Manganese
Zinc
Copper
Molybdenum
Nickle
Cobalt
Silicon
Sodium
Fluoride#
Iodine#
Selenium#
Chromium#

Micro-nutrients found in animals only

Intrinsic

Contamination *

Silica, dirt, soil, limestone, rocks, minerals, other trace element (V, Hg, Pb, As, Cd etc.)

*Natural minerals or contaminants in soil
OR
Introduced during harvesting

External source

Woody biomass

Herbaceous crops

Agricultural waste

Forest residue

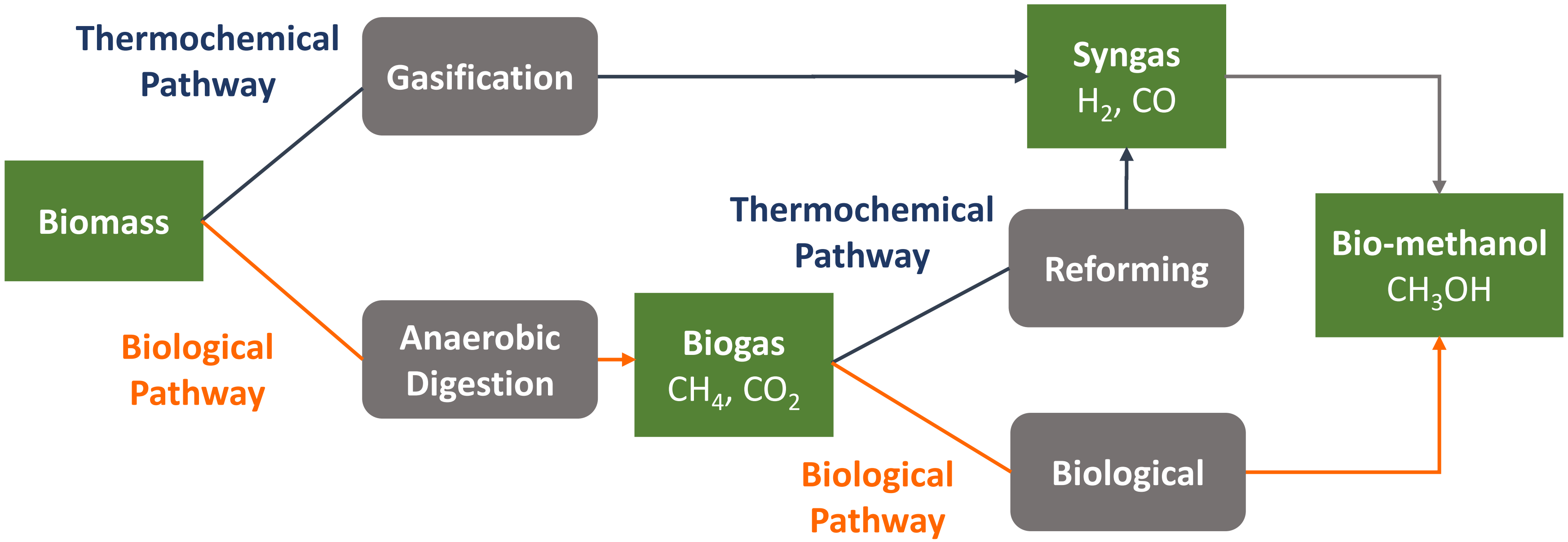
Agri-food industry waste

Livestock manure

Organic municipal waste

Industrial waste, WWTP sludge

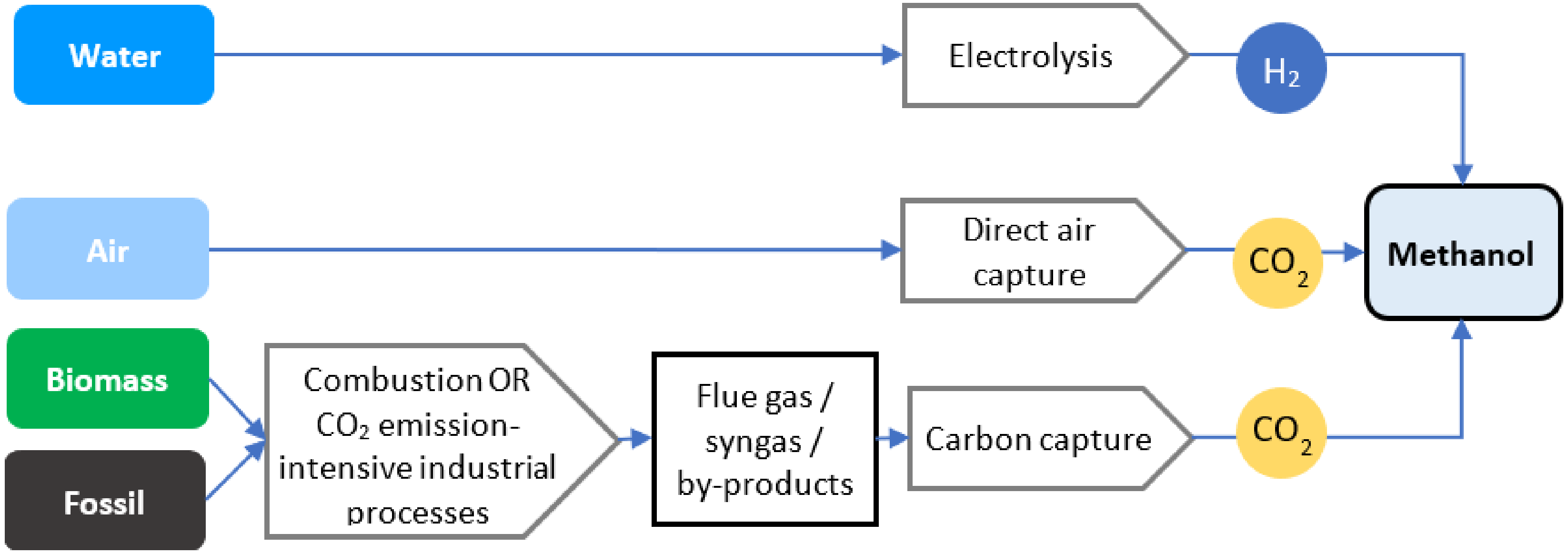
2. Methanol Fuel Quality
- Biomass Feedstock



<u>SEA region</u>

- Abundance forestry and agricultural resources (oil palm frond, empty fruit brunch and trunk, rice straw, sugarcane trash, rice husk, cassava stalk)
- Unutilised residues (2019) - potential to produce 106.98 million tonnes of bio-methanol (≡ 2.13 EJ energy)
- Projection: 122.80 million tonnes in 2050 (27% of global maritime energy demand projected by DNV)
- Industrial waste and municipal waste potential in populated areas

2. Methanol Fuel Quality
- Direct Production Pathways



Direct hydrogenation of *pure* CO_2 and H_2 simplifies MeOH synthesis chemistry. Fewer reactions and by-products

Impurities in H_2 from electrolysis

H_2O, N_2, Argon, CO_2 particulates

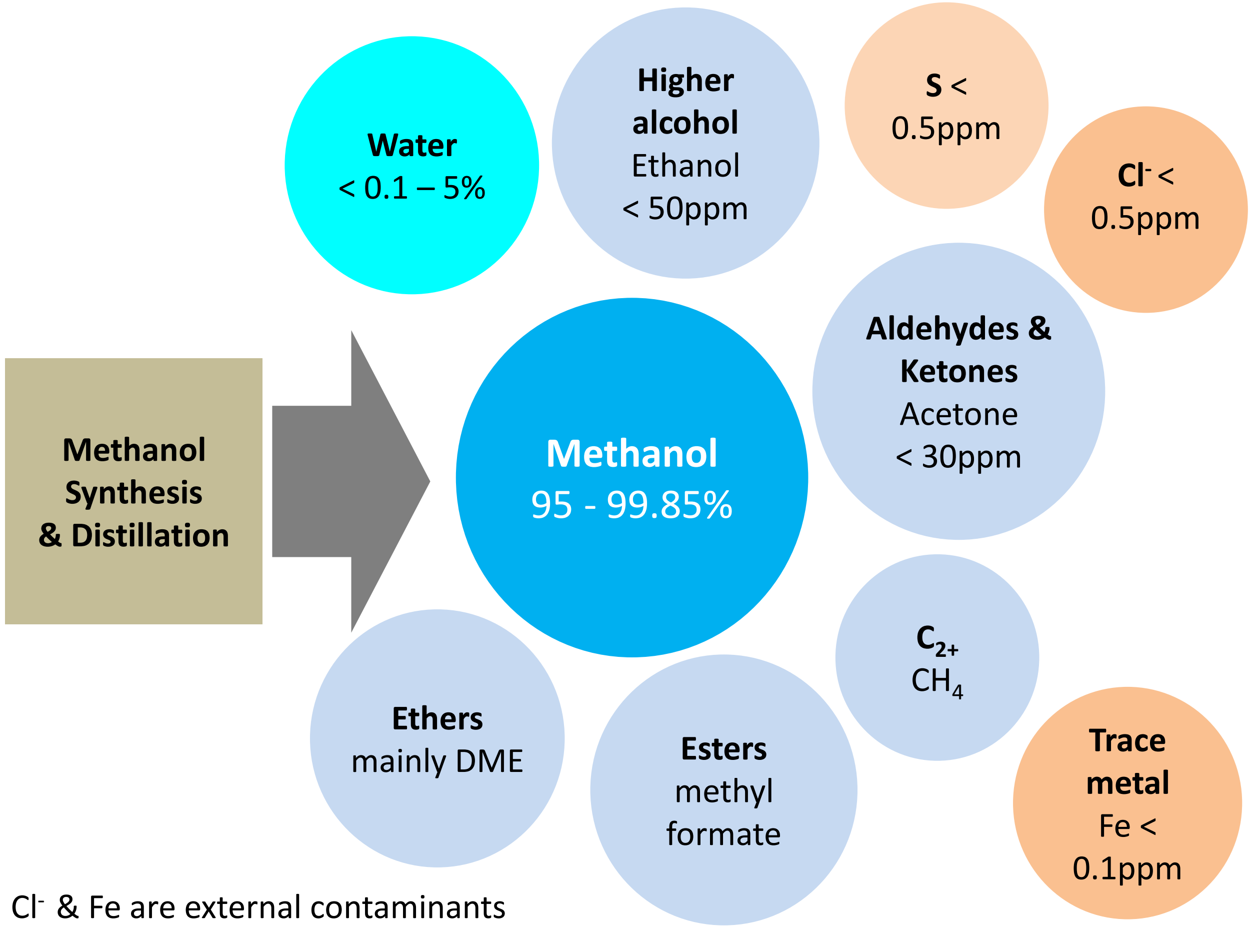
	Impurities in CO_2 from C capture	
Fuel	S, N, halogens, trace metals (Hg, Pb, Se, As) Alkali metals (Cl^-, OH^-, SO_4^{2-} of K and Na) for biomass	
Complete oxidation	Water, SO_x, NO_x, HCl, HF	PM (ash, soot, PAH), Volatiles (H_2, CH_4, C_2H_6, C_{3+})
Partial oxidation	CO, H_2S, COS, NH_3, HCN	
Oxidant / Air ingress	O_2, N_2, Ar	
Process fluids	Glycol, amine, Selexol, Rectisol, NH_3, H_2O.	

CO_2 Purity 95 - 99.95%

H_2 Purity 98 - 99.8%

Less impurities in MeOH

2. Methanol Fuel Quality
- Methanol Purity



* Cl^- & Fe are external contaminants

Bio-methanol

Higher tar in syngas
- Due to lower gasification temperature
- More complex syngas cleaning process (tar reforming)

Higher alkali and alkaline earth metals
- Catalyse formation of higher alcohols, ethers
- More complex distillation processes to remove by-products

E-methanol

Less by-products and impurities

Majority of impurities generated from MeOH synthesis due to high purity syngas / CO_2 & H_2

Crude methanol 96.8% (natural gas) 91.3-95% (woody biomass)

Final purity depends on energy intensive distillation process (15% of production cost)

2. Methanol Fuel Quality

- Methanol Marine Engines Fuel Requirements

	WinGD	MAN	Wärtsilä	ABC	ScandiNAOS / Scania
Engine Type	DF, CI 2-stroke low speed	DF, CI 2-stroke low-speed	DF, CI 4-stroke medium-speed	DF, CI 4-stroke medium-speed	SF, CI 4-stroke high-speed
Pilot	N/A	5%	5 – 8%	30%	3% additives
MeOH	N/A	95%	92 – 95%	70%	97%
Purity	95%	95%	99.85%	N/A	99.85%
Concept	HP-DI	HP-DI	HP-DI	HCCI-DI or RCCI	HP-DI + ignition additives
MeOH Injection	N/A	HP-DI injector	HP-DI Twin (1 + 3 nozzles)	PFI	HP-DI
Pilot Injection	N/A	HP-DI injector		HP-DI	NIL
Injection Pressure	N/A	550 bar	600 bar	< 10 bar	N/A
NOx (Tier III)	SCR	SCR / water	SCR	SCR/oxi-cat	No post-treatment

Low flashpoint, corrosivity

- Double-walled tanks, piping
- Compatible material
- Safety devices, protocols and procedures, IGF Code (to be revised)

Low lubricity

- Lubrication additives (existing or additional)

Formaldehyde, NOx emissions

- Post-combustion treatment (oxidation catalysts, SRC)

2. Methanol Fuel Quality
- Fuel Cells Fuel Requirements

	PEMFC	DMFC	SOFC
Anode	Pt	Pt-Rd catalyst	Ni
Electrolyte	Polymer membrane	Polymer membrane	Solid ceramic
Temperature (°C)	100 LT 200 HT	60-130	800-100
Fuel	H2	Methanol	HC to syngas

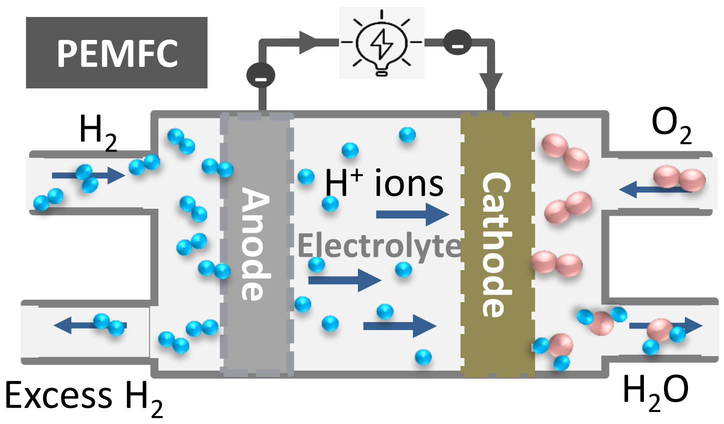
Impurities

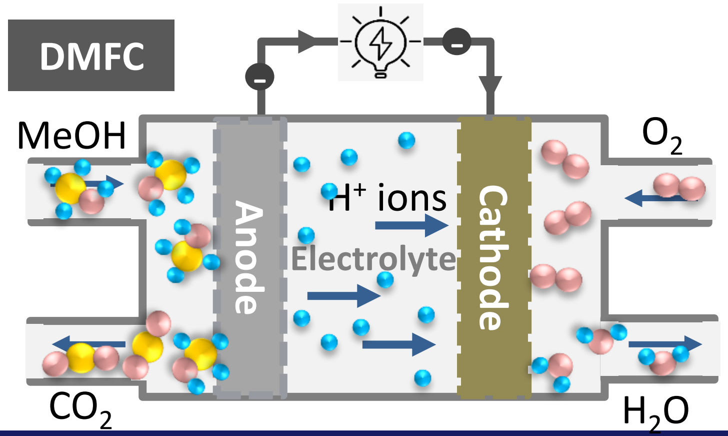
- **Block** (deposition) or **occupy** active sites on catalyst (adsorption)
- **Damage** or degrade electrode and electrolyte
- **Block** or **deviate** electrochemical reaction pathway

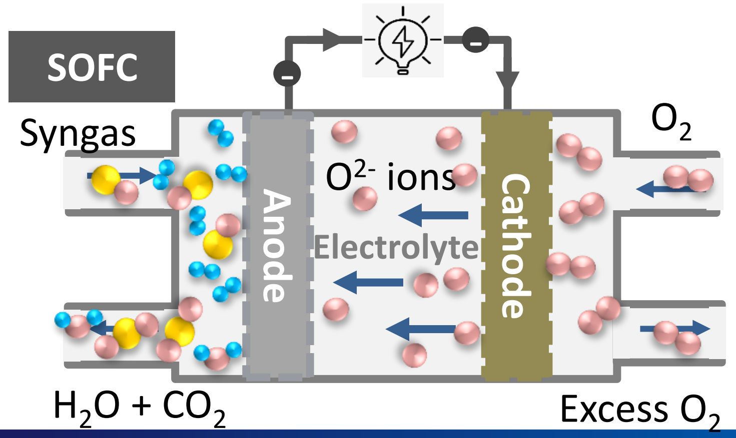
ISO 14687 Hydrogen and hydrogen-based fuel (reformate) PEMFC
CO, NH_3, Cl^-, S, HC, Na, K, Fe, HCHO

Acetone, acetic acid & higher alcohol – compete for active sites on catalyst, inhibit electrochemical reactions

Cl^-, S, B – adsorption & reaction with Ni
siloxane, HC – deposition

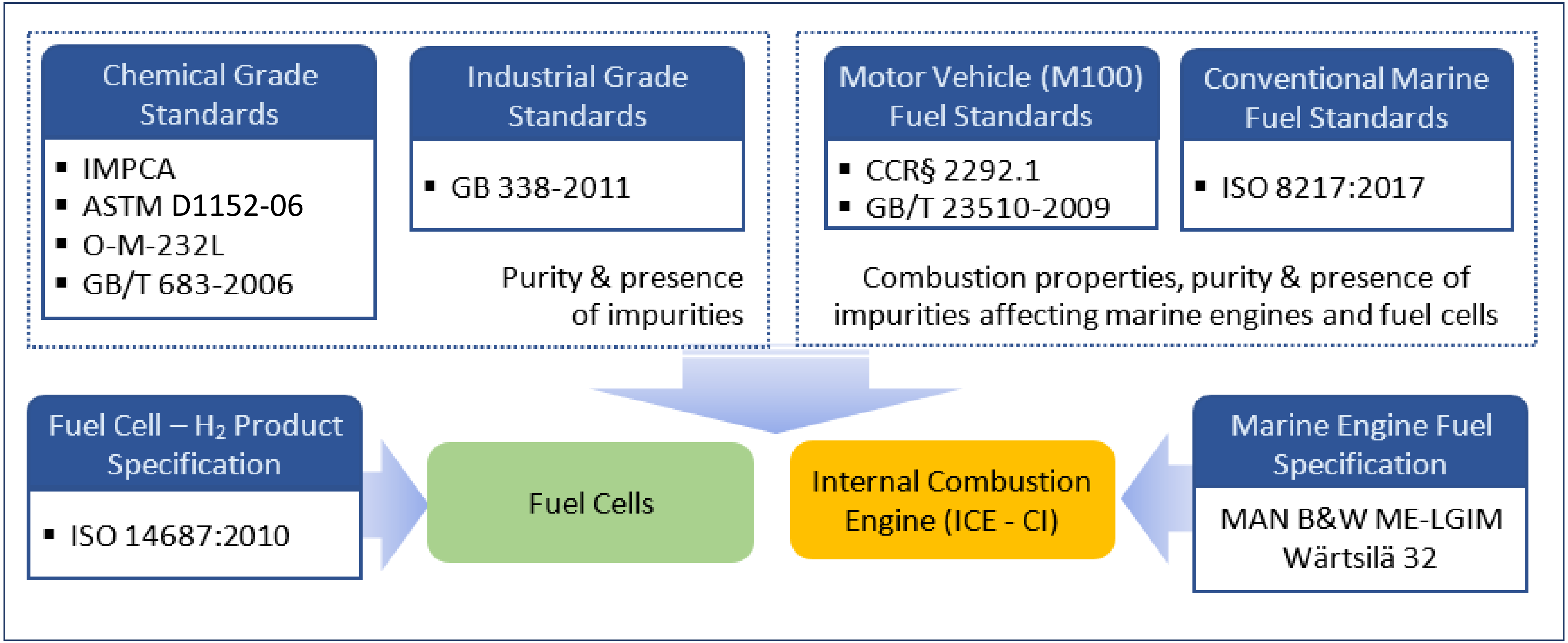






2. Methanol Fuel Quality
- Existing Standards & Specifications

- Existing standards for **chemical & industrial**, gasoline-methanol fuel blends & pure methanol fuel in **ground vehicles**
- Currently no specifications on methanol as a **marine fuel**
- **ISO/AWI 6583 Specifications of methanol as a fuel for marine application** is under development (committee stage)



2. Methanol Fuel Quality
- Comparison of fuel standards and specifications

Methanol for Chemical & Industrial

Physical Properties

Methanol Content, **Density**, Distillation Range, **Water**, **Appearance**, Colour

By-Products

Ethanol, **Acetone**, Aldehydes + Ketones, Carbonyl Compounds

Chemical Properties

Carbonizables, Permanganate Time/Content, Non-volatile Matter, Evaporation Residue, Total **Acidity**/Alkalinity

Contaminants

Sulphur, **Chloride**, Iron

Methanol for Motor Vehicle

Physical Properties

Methanol Content, **Density**, Distillation Range, **Water**, **Appearance**

By-Products

Other Alcohol & Ethers, Other Hydrocarbons

Chemical Properties

Gum, Non-volatile Matter, Evaporation Residue, Total **Acidity**/Alkalinity

Contaminants

Sulphur, **Chloride**, Sodium, Lead, Phosphorous

Methanol for Marine Engine (MAN)

Physical Properties

Methanol Content, **Water**, **Lower Calorific Value**, **Appearance**

By-Products

Ethanol, **Acetone**

Chemical Properties

Acidity

Contaminants

Sulphur, **Chloride**

Conventional Marine Fuel

Physical Properties

Viscosity, **Density**, Cetane Number / CCAI, Flash Point, Pour Point, Cloud Point, **Water**, **Appearance**, Lubricity

Fuel Stability

Acid Number, Total Sediment, Oxidation Stability, FAME

Combustion Residue

Carbon Residue, Ash

Contaminants

Sulphur, Hydrogen Sulphide, Sodium, Vanadium, Al + Si, Used Lubricating Oil, Ca + Zn, Ca + P

2. Methanol Fuel Quality
- Proposed specifications & reportable parameters

Physical	
Methanol Water Appearance Colour	Quick purity assessment
Flash Point* Viscosity* Lubricity*	Safety & operational
Distillation range* Density*	Indicate purity

***Changes with water content**

Combustion	
Lower heating value*	Engine efficiency

Density* and Lower heating value* → Commercial settlement

Carbon Tracing	
Fossil vs non-fossil	Identify renewable & low carbon methanol

Boiler & External Combustion Engine
> 90% purity

Internal Combustion Engine
> 95% purity

Fuel Cell Grade
> 99.9% purity

Besides ISO14687, CO, formaldehyde, formic acid, siloxane and specific trace elements (K, Fe, B) may be required depending on manufacturers specifications.

By-products	
Acetone Ethanol Other alcohol, ether	Combine as other alcohol, ether
Other hydrocarbons	→ BETX contamination
Total acidity Total particulates	Contamination, degradation Wear & tear, plugging, corrosion indicator

Inorganic	
Sulphur	→ Regulatory
Sodium Chloride	Seawater contamination, Cl ions contribute to corrosivity of methanol

Methanol Engine Technology and Development Progress

Overview of Ignition Strategies

Combustion Concepts for Methanol CI Engines

Current Status

3. Methanol Engine Technology and Development Progress

- Overview of Ignition Strategies

- **Injection method** (high or low pressure, direct injection or port fuel injection)
- **Injection timing** (intake, compression, in-between, near TDC)
- **Pilot / Dual Fuel** (high reactivity fuel for ignition, promote autoignition)
- **Assisted ignition** (spark, ignition improvers)
- **Exhaust Gas Recirculation / inlet air heaters**
- **Compression ratio**

Dual Fuel
Reactivity Control (modified PPC) (40% Methanol)

Homogeneous Charge-Direct injection (90% Methanol)

High Pressure-Direct Injection (95% Methanol)

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Single Fuel
Homogeneous Charge (HC)
Spark ignition

↑ Efficiency
↓ Emission

SI Engine
Otto Cycle

Single Fuel
Premixed charge (PC)
Partially Premixed Charge (PPC)
Stratified Charge (SC)

CI Engine
Diesel Cycle

Promote auto-ignition

Low — Fuel reactivity — High

High Octane, Prevent autoignition
NG, biogas, MeOH, EtOH, LPG, Gasoline

High Cetane, Promote autoignition
Diesel

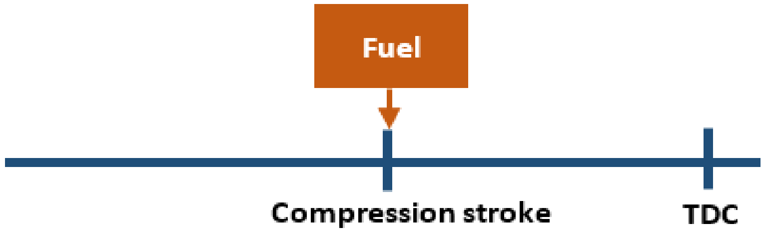
3. Methanol Engine Technology and Development Progress
- Single Fuel CI Combustion Concepts

HCCI
Homogenous **C**harge **C**ompression **I**gnition

PFI or DI at intake. EGR.
Compressing a homogenous charge (SI charge intake) to autoignition temperature (CI ignition process).

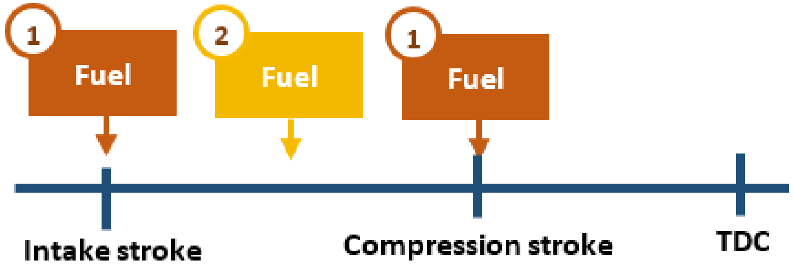
PCCI / PPCI
Premixed **C**harge **C**ompression **I**gnition

DI between HCCI and CI. Hybrid of HCCI and CI. EGR.
Shorter mixing time, less homogenous combustion.



SCCI
Stratified **C**harge **C**ompression **I**gnition

① PFI for part of the fuel at intake, the rest DI at compression OR
② DI anytime between intake and compression
Hybrid of HCCI and CI. Stratified combustion. Ignition at locally rich zone and proceed to locally leaner zones



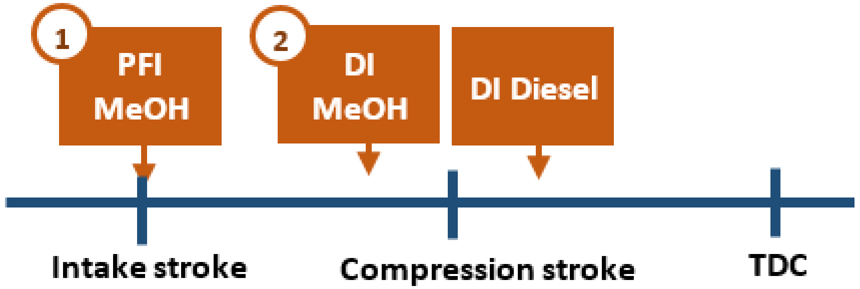
SICI
Spark **I**gnition **C**ombustion **I**gnition

PFI at intake. Hybrid of HCCI and SI.
Fuel ignited by spark. Energy released increases T and P to auto-ignition conditions for CI combustion

3. Methanol Engine Technology and Development Progress
- Dual Fuel CI Combustion Concepts

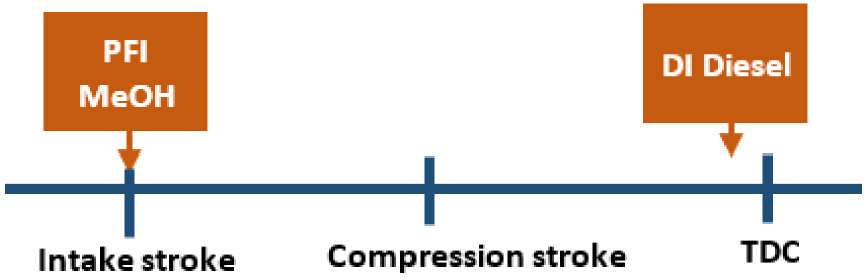
RCCI
Reactively **C**ontrolled **C**ompression **I**gnition

Variation of PCCI and PPCI using dual fuel. EGR.
Adjust mass ratio of HRF and LRF to control autoignition and combustion
①PFI or ②Early DI of MeOH to form premixed charge
DI of diesel at early or middle of compression stroke.
Variations: 2 DI of diesel. First diesel DI to enhance reactivity of fuel mixture, second diesel DI creates stratification.
Methanol substitution ~ 50-60% (~ 40% for Chinese engine)



HCCI-DI
Conventional Dual Fuel

PFI MeOH with air to form homogenous charge.
DI of diesel near TDC for ignition of homogeneous charge.
Main fuel energy: MeOH
Ignition energy: Diesel
Methanol substitution ~ 90% (90% for Chinese engine)



Dual Fuel HP-DI
High **P**ressure **D**irect **I**njection, non-premix

HP-DI of diesel to create high T and P for MeOH ignition
HP-DI of MeOH and diesel to enhance atomisation
Injection near TDC
Center methanol injector, off-centered diesel pilot injector
Methanol substitution ~ up to 95%

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MAN Energy Solutions

3. Methanol Engine Technology and Development Progress

2-stroke, low-speed marine engines for large ocean-going vessel

- Commercially available
- Methanol replacement ratio up to 95% with HP-DI
- Retrofit packages for existing engines available

4-stroke, high-speed engines for small vessels

- Development slower, converting from existing diesel engines.
- Methanol replacement ratio ~ 30 to 40% with low-pressure PFI
- Constraints due to size and complexity of high-pressure injection system
- Exception:
    - Scania single-fuel engine with 3% MD97 additives to overcome ignition and lubricity issues, cost effectiveness

4-stroke, medium speed engines for larger vessels

- New-build and modified engines available commercially.
- Methanol replacement ratio ~ 70 – 95% with HP-DI

Conclusion

Methanol as a Marine Fuel

Good combustion properties.

Combustion and non-combustion issues can be overcome.

Methanol Fuel Quality

Methanol from biomass likely to contain more by-products, incurring additional cleaning and purification cost. Not an issue if lower purity is acceptable.

Lower purity (crude 90-95%) allows for cost-savings.

Separate specifications based on type of energy converters (external combustion, internal combustion, fuel cells).

Methanol Engine Technology and Development Progress

Low-speed and medium-speed engines available for larger ocean-going vessels, with high replacement ratio.

Further improvement in replacement ratio and cost competitiveness of high-speed engines for smaller vessels.

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