NEXT SHALE 2017

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Navigating the Future of Unconventional Resources

High CO_2 shale gas conversion to value-added products

Advisian

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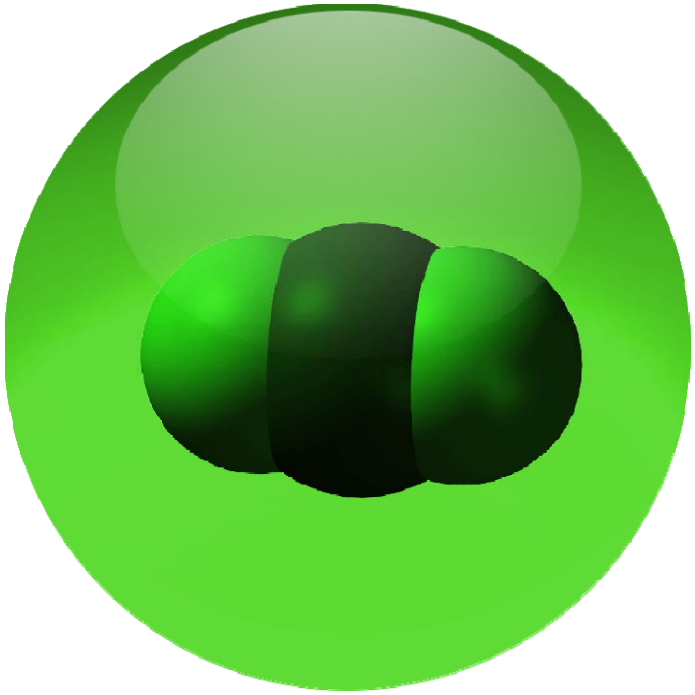
NS17 – 120

Background

- The province of British Columbia claims vast reserves of shale gas which could potentially be used as feedstock for the LNG industry
- Kitimat LNG and LNG Canada, planned to use the high CO_2 shale gas from Liard and Horn River areas as feedstock
- CO_2 content of the shale gas varies between 8% for Liard and 12% for Horn River.
- Typically CO_2 is stripped down to about 2% at the upstream gas processing plant, with balance being removed at the liquefaction plant

How to deal with removed CO_2 in the upstream process?



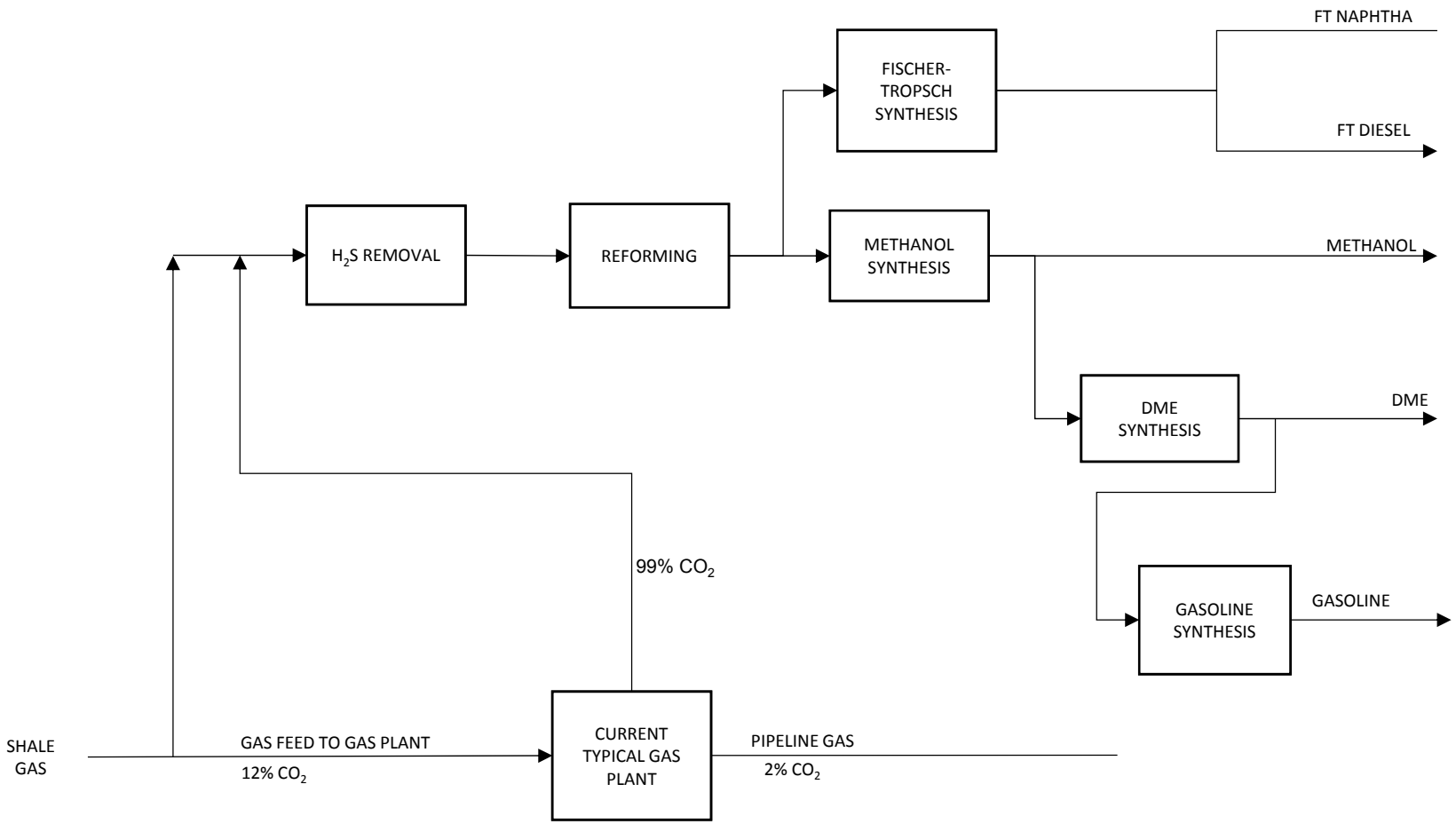
- The options in dealing with CO_2 removed at the upstream facilities from the shale gas are:
  - Discharge to atmosphere
  - Compression and Sequestration
  - Conversion to value-added Products
- The first option is questionable from the environmental point of view
- The second option is costly, technically difficult, and does not add any value
- CO_2 conversion to value added products seems to be an attractive option from environmental and carbon retention standpoint

Utilization Alternatives

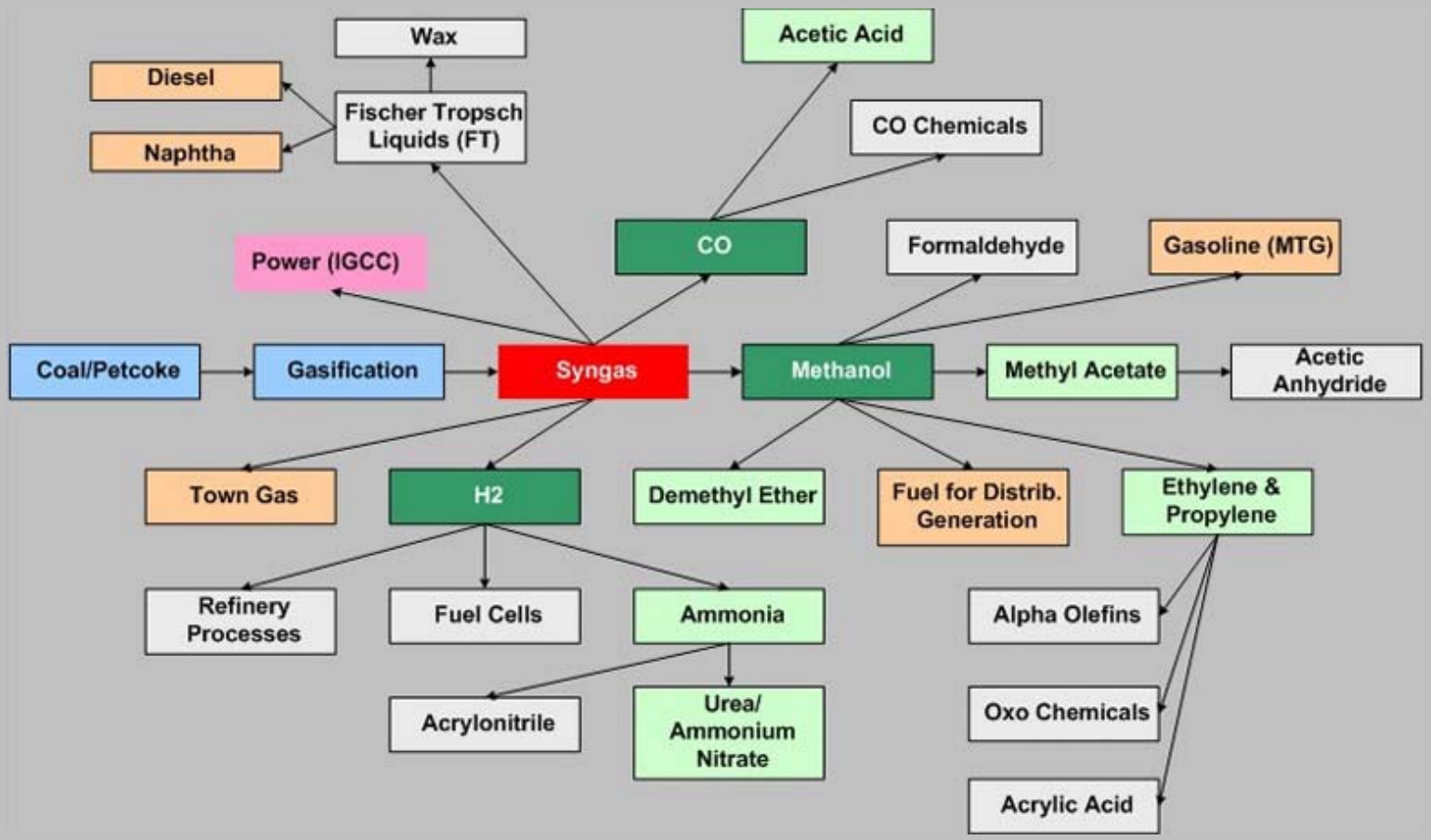
- Basic utilization concept:
  - CO_2 off-gas from gas sweetening operations is combined with the high CO_2 shale gas
  - The mixed gas is then fed to a reformer that generates syngas, (CO/H_2 mixture)
  - Syngas is then catalytically converted into various products
- A modified steam-methane-reformer, (SMR) is capable of accepting high CO_2 content in the feed gas, (up to 30-40%).
- Two proven syngas catalytic conversion options are considered:
  - Fischer-Tropsch Synthesis
  - Methanol/DME/Gasoline Route

Sasol-Oryx Plant: Fischer-Tropsch synthesis, Qatar

Concept Block Diagram



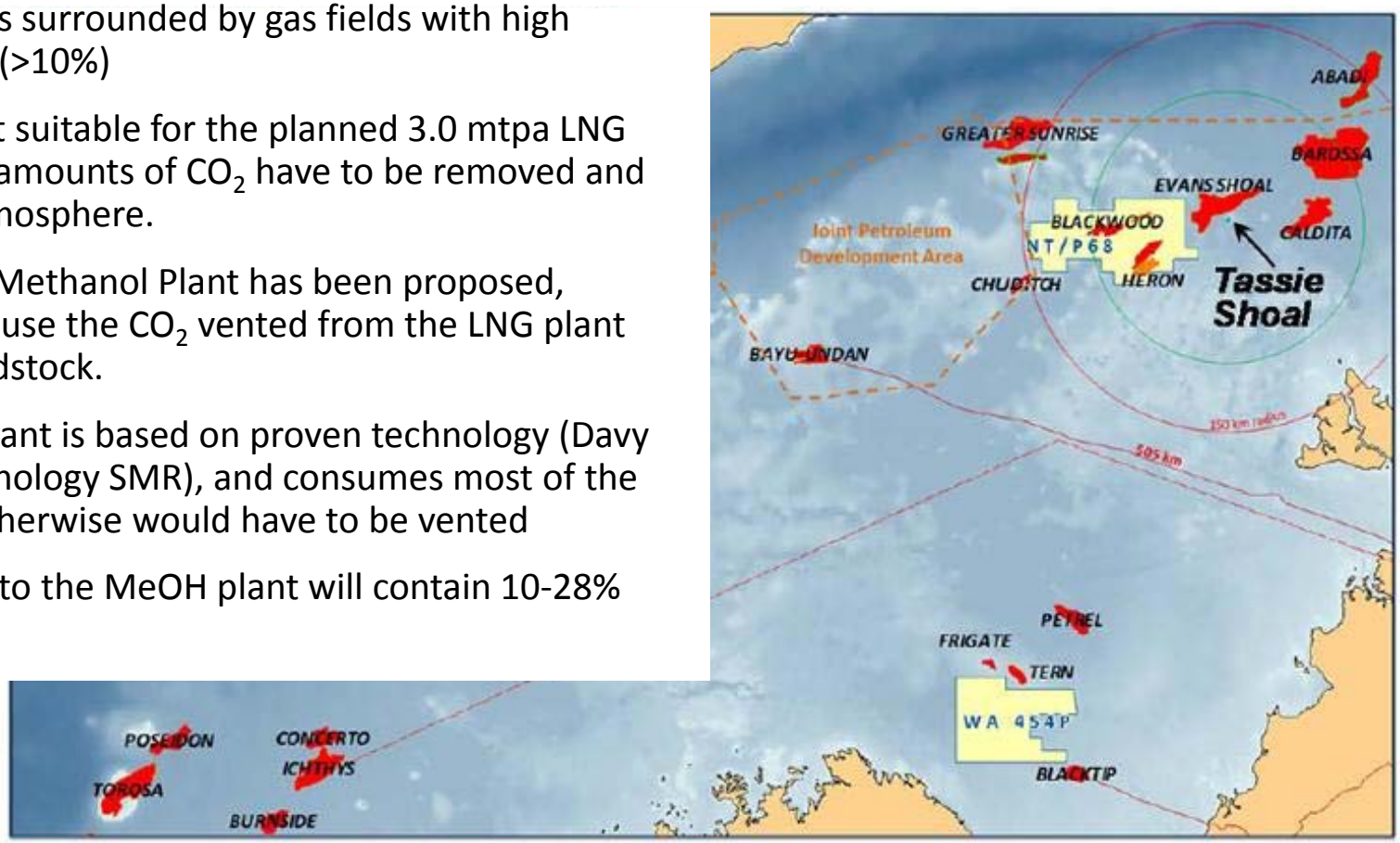
Syngas Utilization Options



Tassie Shoal Methanol: Australia

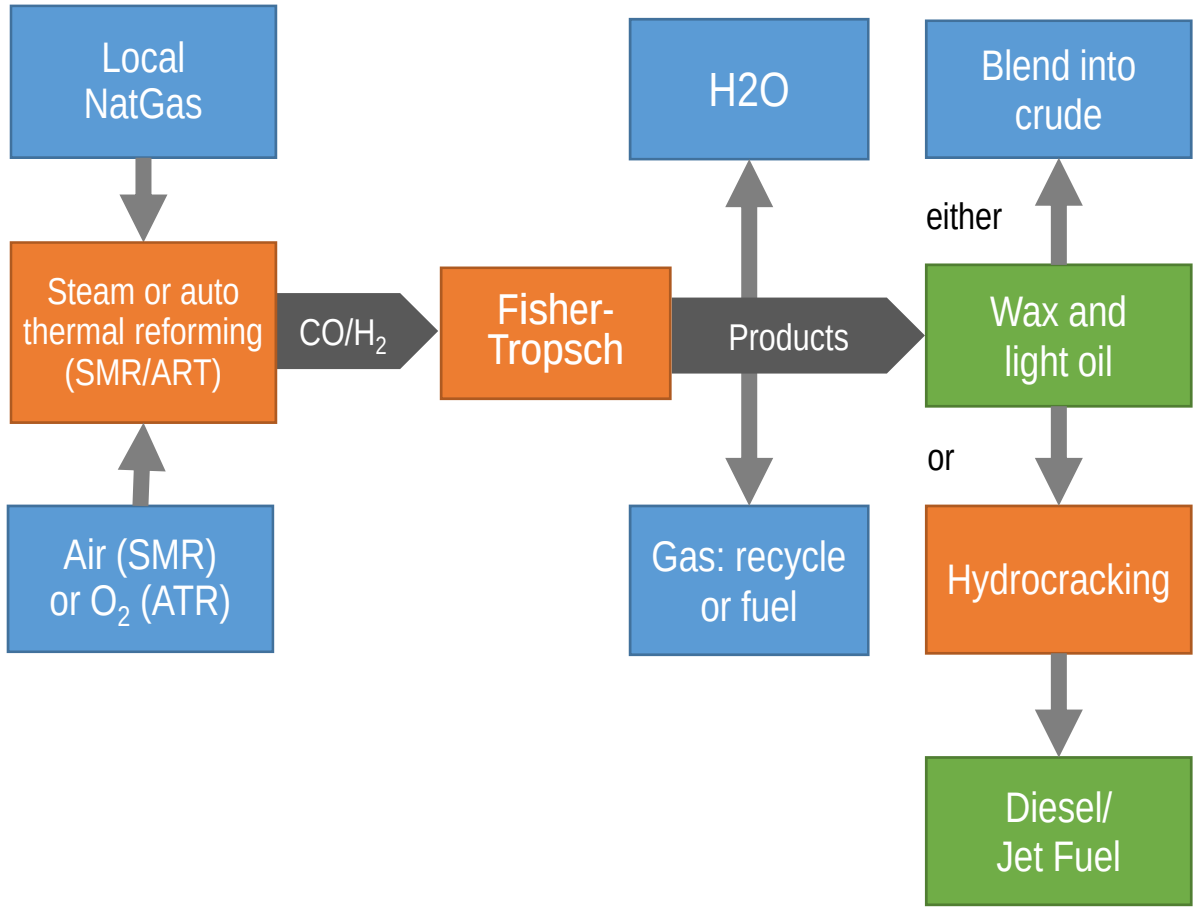
(Similar to BC Shale Gas)

- Tassie Shoal is surrounded by gas fields with high levels of CO_2 (>10%)
- The gas is not suitable for the planned 3.0 mtpa LNG plant. Large amounts of CO_2 have to be removed and vented to atmosphere.
- A 1.75 mtpa Methanol Plant has been proposed, which would use the CO_2 vented from the LNG plant feed as a feedstock.
- The MeOH plant is based on proven technology (Davy Process Technology SMR), and consumes most of the CO_2 which otherwise would have to be vented
- The gas feed to the MeOH plant will contain 10-28% CO_2



Fischer-Tropsch (FT) Process

- Initially iron-based catalyst, currently mostly cobalt-based catalyst
- Cobalt-based catalyst can handle a wider range of H_2/CO ratios in syngas
- Operating conditions in F-T reactors are typically 430˚F to 480˚F and 290 to 360 psig depending on the product slate
- Products are paraffinic naphtha and high-cetane (>70) paraffinic sulphur-fee diesel

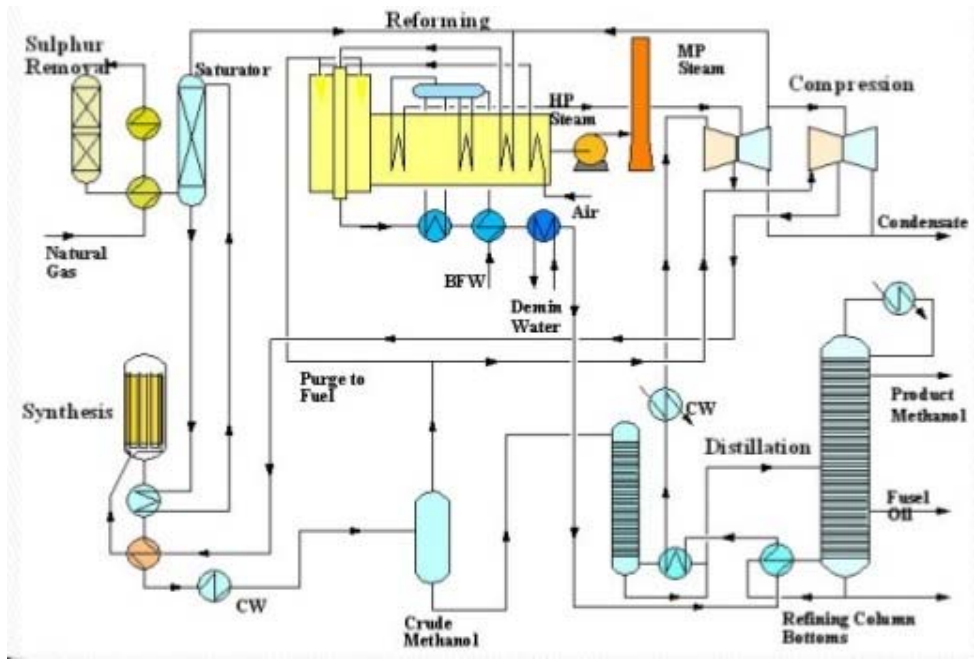


FT Products Typical Properties

Properties		Spec
C3/C4 Condensate		
Vapor Pressure @ 37.8˚C	kPaa	1434
C5+	% v	< 2.0
Free Water Content		none
Naphtha		
Cut Range	˚C	C5 - 149
Density	˚API	74.5
Reid Vapor Pressure	kPaa	69 (max)
Paraffin Content	%	~ 100
Diesel		
Cut Range	˚C	149 - 343
Density	˚API	54
Flash Point (closed PM) at 1 atm.	˚C	54 (min)
Cold Filter Plugging Point	˚C	- 10
Sulphur Content	ppmw	< 1
Cetane Number		75 - 80

Methanol

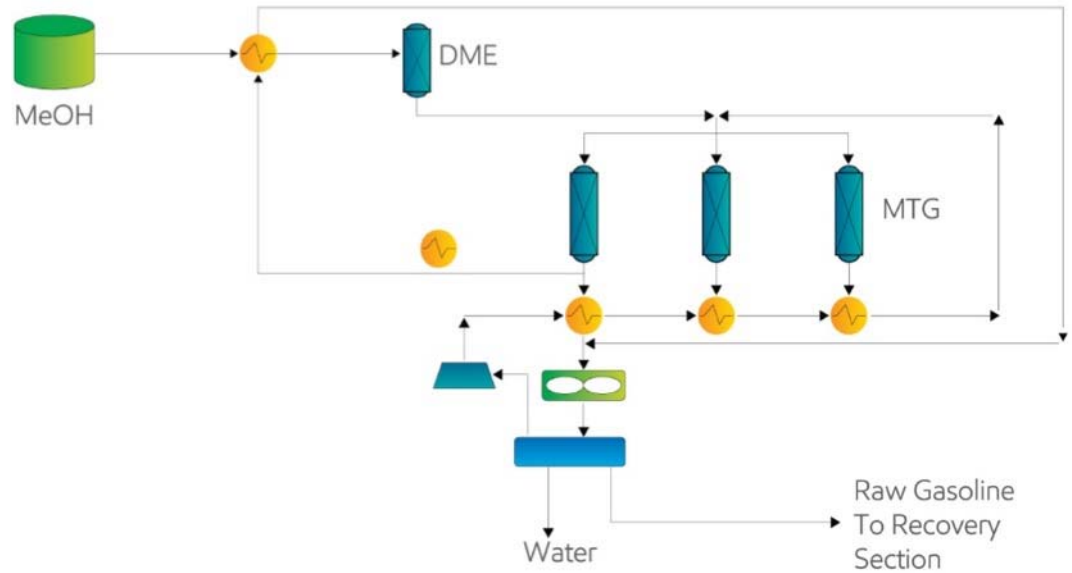
- Methanol process consists of the following steps:
  - Natural gas reforming to syngas (CO, CO_2 & H_2)
  - Syngas conversion to methanol (CH_3OH)
  - Distillation – product purification
- Reforming – steam and methane passing through catalyst filled tubes to form a mixture of syngas, residual methane and water
- Methanol synthesis – syngas reaction over fixed bed catalyst to form methanol
- Distillation – crude methanol is distilled to remove light ends, fusel oil and water



Conventional Methanol Plant Flowsheet

Methanol-to-Gasoline Conversion Section

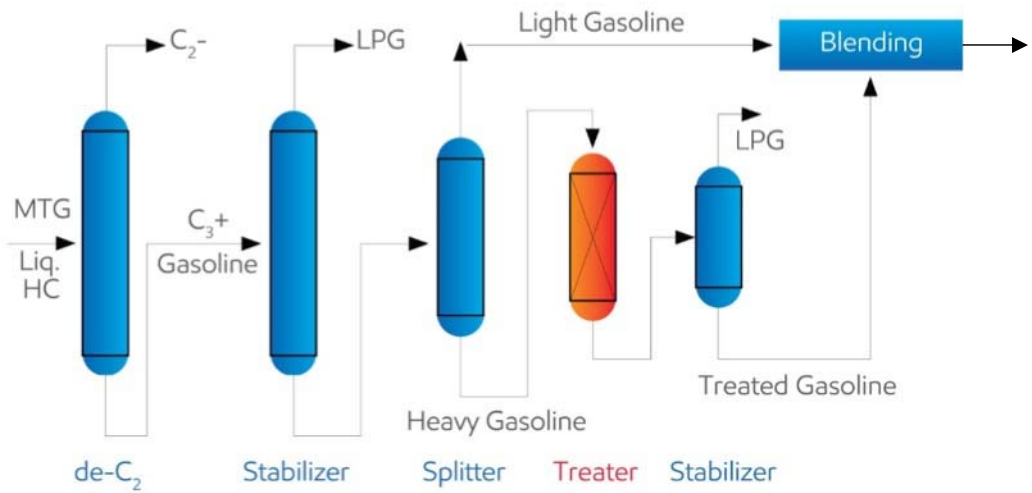
- Methanol is first dehydrated over an amorphous alumina catalyst to primarily form di-methyl ether (DME) and water and some unconverted methanol
- In the MTG reactors, methanol and DME are completely dehydrated by a ZSM-5 zeolite catalyst forming light olefins and water
- Light olefins oligomerize into higher olefins, which combine through various reaction paths into paraffins, naphthenes, and methylated aromatics.
- The shape-selective MTG catalyst limits the hydrocarbon synthesis reactions to about C_{11}.



MTG Reactor Section Process Flow

Methanol-to-Gasoline Gasoline Recovery Section

- The raw gasoline is stabilized, first to remove remaining C_2- gases, followed by a stabilizer column that removes C_3s and C_4s as LPG fractions
- Durene (1,2,4,5-tetramethylbenzene) was formed as by-product during the MTG synthesis
- Treatment is required to meet the maximum durene content (2%)
- Gasoline is split into a light fraction and heavy fraction, the heavy fraction is processed in a mild hydrotreater that reduces the durene content
- Treatment has no impact on yield or octane



New Zealand Synfuels Commercial MTG Plant

MTG Gasoline Properties

(ExxonMobil info)

Table 5

MTG Gasoline Properties / Composition	
Octane, RON	92
Octane, MON	82
(R+M)/2	87
RVP (psi) (1)	9
T (50) F	201
T (90) F	320
Paraffins, vol%	53
Olefins, vol%	12
Napthenes, vol%	9
Aromatics, vol%	26
Benzene, vol%	0.3
Sulfur	nil

(1) Typical is shown. Actual controlled by Stabilization.

Table 3

MTG Gasoline vs US Conventional Refinery Gasoline			
	Summer 2005	Winter 2005	MTG Gasoline
Oxygen (WI%)	0.95	1.08	
API Gravity	58.4	61.9	61.8
Aromatics (% Vol)	27.7	24.7	26.5
Olefins (% Vol)	12	11.6	12.6
RVP (psi)	8.3	12.12	9
T50 (°F)	211.1	199.9	201
T90 (°F)	330.7	324.1	320
Sulfur (ppm)	106	97	0
Benzene (% Vol)	1.21	1.15	0.3

Existing Gas Plant Example – GTL Add-on

Gas Plant		
Shale Gas	250	mmscfd
CO_2 in feed	12	%
	30	mmscfd
CO_2 Removed	26	mmscfd
Residue Gas	224	mmscfd
CO_2	2.00	%

GTL Plant		
Shale Gas	105	mmscfd
CO_2 in feed	13	mmscfd
CO_2 offgas	26	mmscfd
Total feed	131	mmscfd
CO_2 in feed	29.47	%

Products		
Methanol	3,400	tpd
Gasoline	11,300	bpd
FT Naphtha	2,700	bpd
FT Diesel	7,500	bpd

Future LNG Feed Plant – GTL Add-on

Gas Plant		
Shale Gas	750	mmscfd
CO_2 in feed	8	%
	60	mmscfd
CO_2 Removed	46	mmscfd
Residue Gas	704	mmscfd
CO_2	2.00	%

GTL Plant		
Shale Gas	150	mmscfd
CO_2 in feed	12	mmscfd
CO_2 offgas	46	mmscfd
Total feed	196	mmscfd
CO_2 in feed	29.56	%

Products		
Methanol	5,200	tpd
Gasoline	17,100	bpd
FT Naphtha	4,100	bpd
FT Diesel	11,300	bpd

Future Plant – GTL Basic Economics – 5 year simple payback

	FT Plant	MeOH	MTG
	(CAN$ millions)		
EPC CAPEX	$1,544	$1,707	$2,563
Revenue/year	$505	$550	$754
Expenses/year			
OPEX	$54	$68	$103
Natural Gas	$137	$137	$137
CO_2	$4	$4	$4
Total Expenses	$195	$210	$244
Net Revenue	**$310**	**$340**	**$511**
Required Product Price			
Diesel/MeOH/Gasoline	$0.63/l	$290/t	$0.76/l

Future Plant – GTL Basic Economics – 3 year simple payback

	FT Plant	MeOH	MTG
	(CAN$ millions)		
EPC CAPEX	$1,544	$1,707	$2,563
Revenue/year	$707	$777	$1,092
Expenses/year			
OPEX	$54	$68	$103
Natural Gas	$137	$137	$137
CO_2	$4	$4	$4
Total Expenses	$195	$210	$244
Net Revenue	**$512**	**$567**	**$848**
Required Product Price			
Diesel/MeOH/Gasoline	$0.94/l	$410/t	$1.10/l

Final Observations

- All three presented options are technically feasible, all involve commercially proven technologies
- Economic feasibility depends primarily on product prices
- Product marketability will play important role as well
  - FT diesel and MTG gasoline are premium-quality transportation fuels
  - Methanol offers numerous options as intermediate product
- Project developer needs well-funded partner and a supportive banker, projects are capital intensive
- Governments may assist through favourable tax (carbon?) and royalty regimes
- **Consider CO_2 as valuable feedstock, not environmental liability**