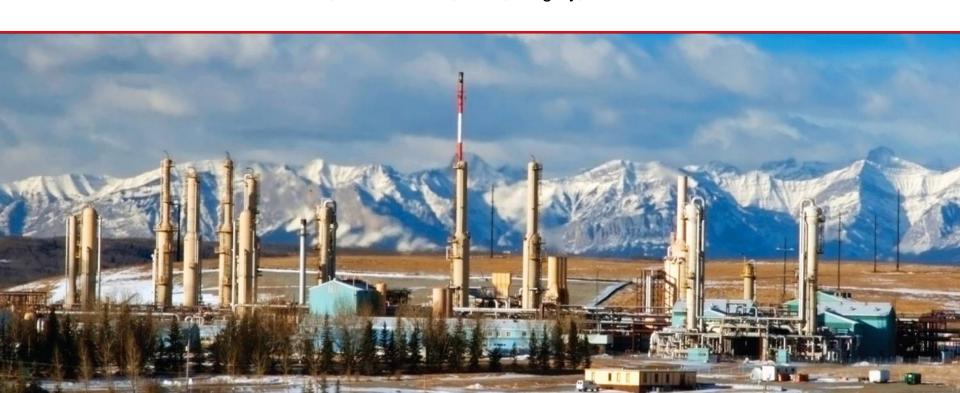
# Alternative Ways to Process and Utilize High CO<sub>2</sub> Content Shale Gas

Jan Wagner and Tanju Cetiner, WorleyParsons Canada GPAC/PJVA Annual Joint Conference, November 14, 2012, Calgary, Alberta



- Introduction
- Typical Shale Gas Processing in Horn River Basin
- Membrane Option to Reduce CAPEX
- Australian Example Tassie Shoal Methanol Project
- ► CO<sub>2</sub> Utilization Alternatives
  - DME and MTG
  - Fischer-Tropsch Liquids
- Final Observations

#### Typical Shale Gas and Pipeline Gas

Typical shale has the following composition:

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• CO<sub>2</sub> 12.0%
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Sales gas specification (TCPL)

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• CO<sub>2</sub> 2.0% max.
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• 
$$H_2S$$
 16 ppm max.

▶ As result for a 400 mmscfd plant 40 mmscfd (2,100 tpd) of CO<sub>2</sub> have to be removed and are typically vented

- Shale gas plant typically consists of the following principal processing steps:
  - Inlet separation and filtration
  - Amine sweetening
  - TEG Dehydration
  - Residue gas compression
- ► For given CO<sub>2</sub> removal and 400 mmscfd gas plant capacity about 4,600 gpm of "MDEA" has to be circulated
- ► TIC for a 400 mmscfd gas plant is around \$500 million
- ► Amine system represents 30% to 40% of TIC

#### Capital Costs associated with amine acid gas removal systems

- Potential option is to use membrane/amine hybrid system
- Based on recent WorleyParsons study 20-30% capital can be saved compared to amine based plant

#### Carbon Dioxide emissions

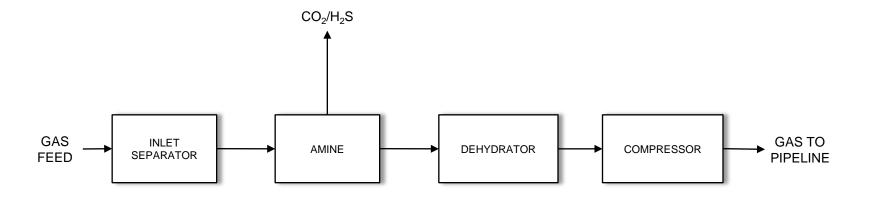
- CO<sub>2</sub> can be utilized to produce synthetic products such as methanol, DME, gasoline or Fischer-Tropsch liquids (naphtha and diesel)
- CO<sub>2</sub> offgas will be mixed with additional shale gas, steam and oxygen for reforming into syngas



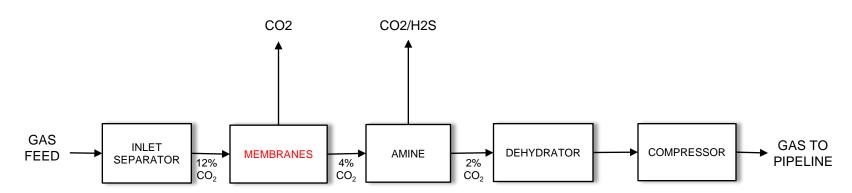
## Membranes in Acid Gas Removal Application

- ▶ Using membranes for CO₂ removal is state of the art technology (polymer based, flat sheet or hollow fibre)
- Membrane process is environmentally attractive and offers cost and operational advantages
- ▶ Membranes remove CO₂ and water, however, do not meet H₂S pipeline specifications
- Additional drawback is the methane loss to permeate, this can be mitigated by installing a multi-stage system (typically 2-stage)
- ► These membranes shortcomings can be overcome through combining with other acid gas removal technologies (e.g. amine) – "hybrid systems"

#### **Amine Sweetening Option**



#### **Hybrid Sweetening Option**





#### 400 mmscfd Shale Gas Plant Example

Amine Based System

Amine circulation rate 4,600 usgpm

Capital Costs \$510 million

Hybrid System

Amine circulation 1,180 usgpm

Capital Costs \$360 million

Hybrid System Design Parameters

Membrane CO<sub>2</sub> removal 12 to 4%

Two-stage system, methane loss less than 3%

Permeate is absorbed in fuel system

 Amine CO<sub>2</sub> removal 4 to 2% and H<sub>2</sub>S removal pipeline specification (4 ppm)



### Convert CO<sub>2</sub> (GHG) To Value Added Products

Natural Gas Feedstock and Value Added Utilization of CO<sub>2</sub> in the Production of Petrochemicals

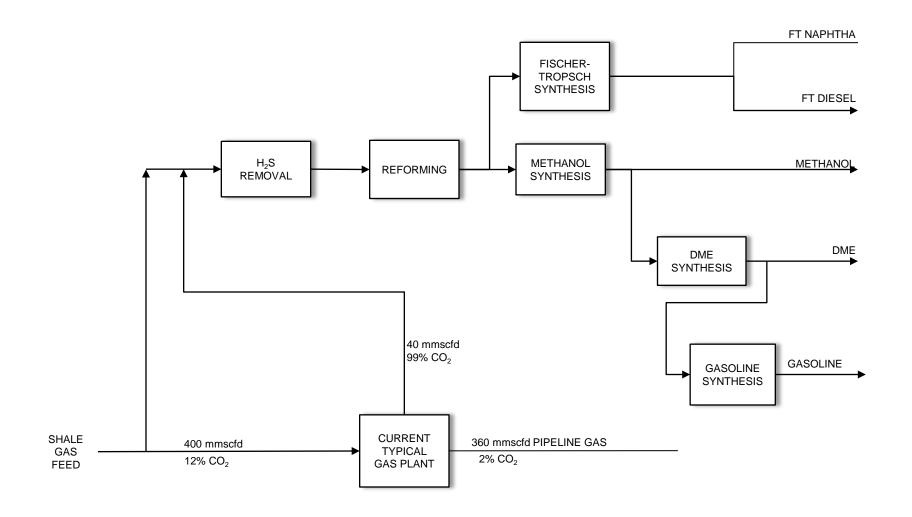


#### High CO<sub>2</sub> Content Gas Utilization Examples

- ▶ Tassie Shoal Methanol Development
  - Tassie Shoal is surrounded by gas fields with high levels of CO<sub>2</sub> (>10%)
  - 1.75 MTPA Methanol Plant is proposed in parallel to commercialize high CO<sub>2</sub> regional resources and CO<sub>2</sub> vented from LNG plant feed
  - The MeOH plant is based on proven technology (Davy Process Technology SMR) and utilizes to maximum practical extent CO<sub>2</sub> which otherwise would have to be vented
  - Gas feed to the MeOH plant contains 10-28% CO<sub>2</sub>
  - This situation is very similar to the Horn River shale gas cases
- ► Maui Gas Fields with CO₂ content in New Zeeland for Methanex's Waitara Valley Methanol since 1980s
- Kapuni Gas Fields for Motuni Gasoline Plants



## Methanol Derivatives and Fischer-Tropsch Products





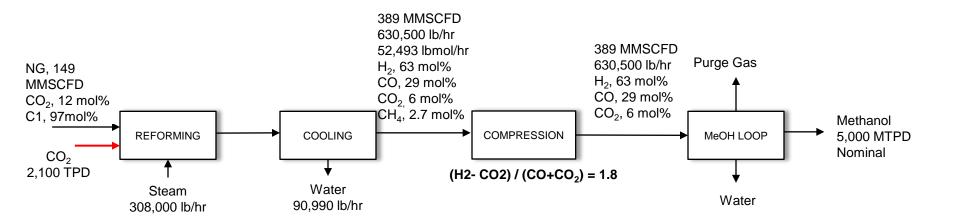
#### Synthesis Gas Production Technologies

- Synthesis Gas (H<sub>2</sub> + CO) which could include CO<sub>2</sub>
- Current Synthesis Gas production Technologies include:
  - Steam Methane Reforming w/ or w/o CO<sub>2</sub>
  - Partial Oxidation
  - AutoThermal Reforming w/ O<sub>2</sub>
  - Combined Reforming
- Reforming technologies under development:
  - Ceramic Membranes w/ or w/o CO<sub>2</sub>
  - Compact Reformers
- Key technology providers: Sasol, Shell, Axens, Haldor Topsoe, Davy PowerGas, Toyo, KBR, Lurgi, Linde, Mitsubishi, etc.
- ► EPC contractors: WorleyParsons, Uhde, Fluor, Bechtel, Jacobs, Deawoo and others will engineer and build synthesis gas, methanol, DME and gasoline plants under licenses of others.



### WorleyParsons Injecting CO<sub>2</sub> at SMR for Methanol Production

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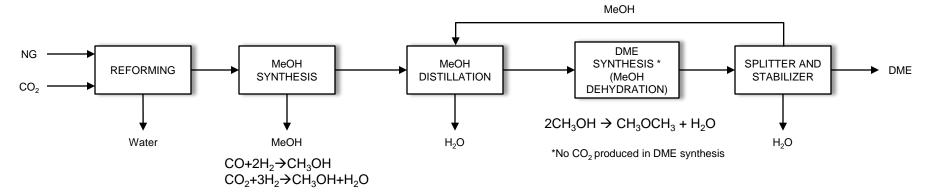


#### **Overall Mass Balance**

IN	lb/hr	OUT	lb/hr
NG	294,000	Syngas to MeOH	630,500
Steam	308,000	Water	154,500
CO <sub>2</sub>	195,998	Purge	12,498
Total	797,998		797,498

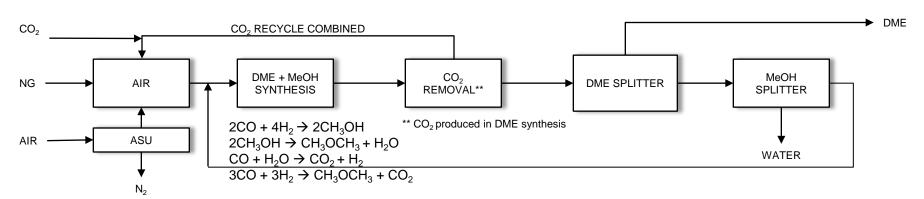
#### NG Feedstock to GTL - DME Processes

#### Two Step Process (Catalytic Dehydration of Methanol)



Material Balance: NG 150 MMSCFD → 5000 MTPD MeOH → 3500 MTPD DME

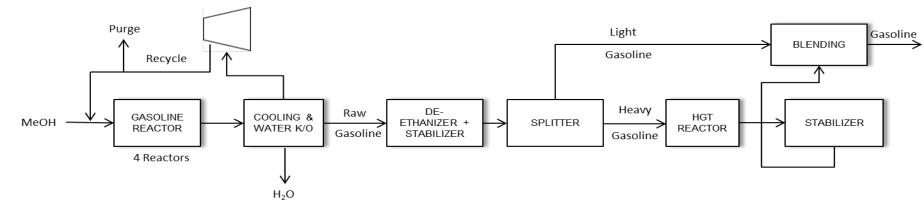
#### One Step Process - Direct Synthesis Route - Typical



Material Balance: NG 150 MMSCFD → 3400 MTPD DME



#### Methanol-to-Gasoline (MTG)



- ► In the first part, methanol is dehydrated to an equilibrium mixture of methanol, dimethylether and water. Water gets knocked out.
- In the second step, the methanol and DME equilibrium mixture is passed over ZSM-5 catalyst to produce hydrocarbons in gasoline boiling point range (C4 to C10) and consists of highly branched paraffins, olefins, napthenes and aromatics.
- ► The gasoline product is similar in composition and volatility and meets gasoline specifications with octane number (RON+MON/2) of 88.

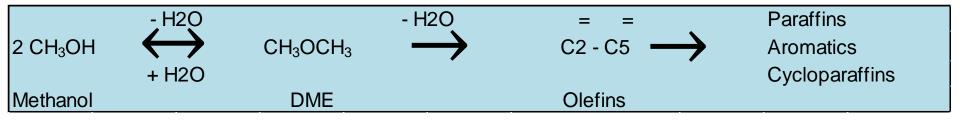


## Methanol-to-Gasoline (MTG) Heat & Mass Balance

<u>Methanol</u>		<u>Gasoline</u>		<u>Water</u>
nCH <sub>3</sub> OH	$\rightarrow$	$(CH_2)_n$	+	$nH_2O$
100 Kg	$\rightarrow$	44 Kg	+	56 Kg
100 GJ	$\rightarrow$	95 GJ	+	0 GJ
		*5GJ of fuel gas recycle to fuel system		

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149 MMSCFD  $\rightarrow$  5,000 MT  $\rightarrow$  2200 MT(16,500 BPD) + 2800 MT

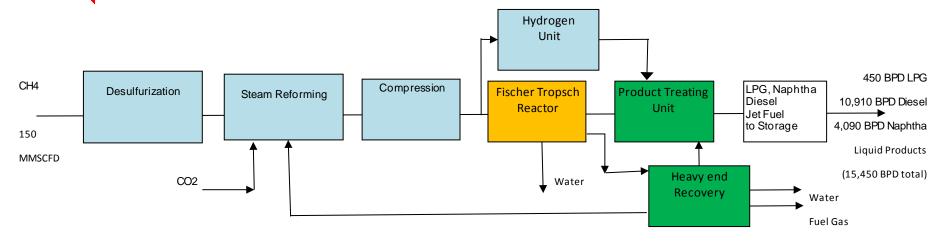


NG Feed + CO2 + Steam → SMR or ATR or POX → Syngas

- → Methanol Synthesis → DME Reactor → Gasoline Reactor
- → Splitter → Gasoline Product

#### Gas-to-Liquids (GTL) – Fischer Tropsch

Simplified Typical Fischer Tropsch Configuration



- The cooled synthesis gas feeds the LTFT reactor, entering at the bottom of the slurry bed of liquid hydrocarbons and F-T catalyst. It is converted into paraffinic hydrocarbon chains via the exothermic F-T synthesis reaction: CO + 2H₂ → -CH₂⁻ + H₂O
- ► The exothermic reaction inside the LTFT reactor is cooled by steam and the MP steam generated.



#### Gas-to-Liquids (GTL) – Fischer Tropsch

- ► The heavier fractions are removed from the slurry and fed into the product work-up unit, licensed by Chevron.
- ▶ Proprietary hydrocracking and fractionation techniques, known and proven in the refining industry, are used to break down these long-chain hydrocarbons into the required product slate of GTL diesel (70–80%) and naphtha (20–30%).

#### Gas-to-Liquids (GTL) Proven Technologies

- These are all commercially proven technology steps.
- XOM MTG plant (2 trains) in NZ has been in operation since 1980s.
- Two GTL plants using the Fischer Tropsch (F-T) process are located in South Africa operated by Sasol and PetroSA (under Sasol licence) and one in Malaysia, operated by Shell.
- ORYX GTL 34,000 bpd, a joint venture between Qatar Petroleum and Sasol with approximate TIC of \$950MM which employs Cobaltbased catalyst in the new generation Slurry Phase Distillate process.
- Shell Pearl Project in Qatar (120,000 bpd) GTL Plant
- Sasol plans 96,000 bpd GTL plant in Alberta



#### **Overview Comparison**

	Capacity		Typical	Current	Energy Efficiency
	MTPD	TIC, \$MM	Cost of Production	Market Price	
			at 2.25 \$/MMBTU		
		(based on 150 MMSCFD gas feedstock)			
Methanol Plant	5,000	\$250	120 \$/MT	420 \$/MT 1.27 \$/Gal	26.5 - 27.5 MMBTU/MT
DME Plant	3,500	\$500	140 \$/MT	600+ \$/MT	40.5 MMBTU/MT
Gasoline Plant	2,200 16,500 BPD	900+	~220 \$/MT	750 \$/MT 100 \$/Bbl	60 MMBTU/MT
Fischer Tropsch to Liquids	1,850 (15,450 BPD)	\$600	~225 \$/MT	750 \$/MT 100 \$/Bbl	70 MMBTU/MT 8.5 MMBTU/Bbl of total liquid product

- Using membranes for gas separation, especially for CO<sub>2</sub> removal, is state of the art technology
- For every project a sweet spot for a hybrid membrane/amine system can probably be found
- ► All value added technologies are commercially proven and can be effectively used to combat GHG emissions (CO₂)
- Type of value added option will be project specific depending on economics and political acceptance

- At current North American depressed gas prices almost any of the value added option can be economically attractive
- Present low cost feedstock and healthy margins is an invitation for the comeback of petrochemicals sector
- ► High CO<sub>2</sub> content shale gas is ideally suited for the production of value added petrochemicals

#### Thank You!



#### Contacts and Acknowledgements

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#### Acknowledgements:

- Kirk-Othmer Encyclopedia of Chemical Technology.
- 2. Article compiled by Paul Kooye (Petralgas -Waitara Valley).
- 3. Methanol to Gasoline Process by Sebastian Joseph and Yatish T. Shah Chemical and Petroleum Engineering Department. University of Pittsburgh, Pittsburgh, PA 15261.
- 4. http://www.carbonsciences.com/ExxonMobil.html
- http://www.oryxgtl.com.qa/
- 6. William Echt, UOP LLC: "Hybrid Systems: Combining Technologies Leads to More Efficient Gas Conditioning", 2002 Laurance Reid Gas Conditioning Conference