

ASIAN NITROGEN + SYNGAS CONFERENCE 2012
Kuala Lumpur 9-11 October

***MHI Proprietary CO₂ Recovery Process
for Increasing Methanol Production***

Shinya Kishimoto



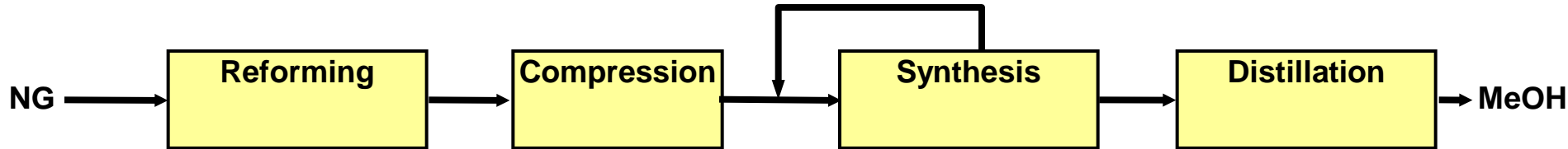
MIES

- 1. Introduction**
- 2. CO2 recovery technology from flue gas**
- 3. CO2 Injection point enhancing methanol production**
- 4. References for methanol production expansion**
- 5. Conclusion**



1. Introduction

Typical Process Scheme of Methanol synthesis



◆ Reforming

- $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$
- $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$

◆ Methanol Synthesis

- $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$
- $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$

$$\begin{aligned} [\text{H}_2] / (3[\text{CO}_2] + 2[\text{CO}]) &= 1.0 \text{ (Stoichiometric)} \\ &= 1.5 \text{ (without CO}_2 \text{ injection)} \end{aligned}$$

By CO₂ injection, this value approaches to 1.0

➔ NG Unit Consumption can be reduced



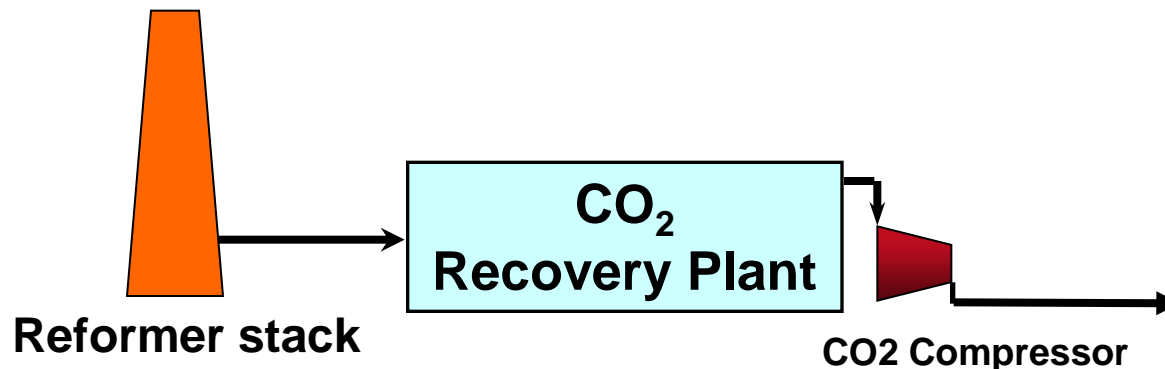
1. Introduction

CO₂ Sources

- ◆ CO₂ removal from NH₃ Plant
- ◆ CO₂ Network Piping
- ◆ CO₂ from Reformer Flue Gas



MHI Proprietary CO₂ Recovery Process



2. CO₂ Recovery Technology From Flue Gas

- ◆ MHI's proprietary flue gas CO₂ recovery technology is named the **KM CDR Process™** (“KEPCO MHI Carbon Dioxide Recovery Process”)
- ◆ MHI proprietary amine solvent **“KS-1™”** with accompanying proprietary equipment achieves reduction of utilities and solvent consumption which leads to lower OPEX
- ◆ This technology is commercially applied since 1999 (10 plants under operation, 1 under construction)
- ◆ World's largest operating flue gas CO₂ recovery plant



2.1 Reference Commercial Plants

- ◆ Ten (10) MHI CDR plants are in operation
- ◆ Mainly in fertilizer plants
- ◆ Easy to operate and high availability



1999
200 t/d
Malaysia



2005
330 t/d
Japan



2006
450 t/d
India



2006
450 t/d
India



2009
450 t/d
India



2009
400 t/d
UAE



2009
450 t/d
Bahrain



2010
240 t/d
Vietnam



2011
340 t/d
Pakistan



2012
450 t/d India



2.2 Process Performance

2.2.1 History of KS-1™ Solvent development

◆ Evaluation of MEA

- MEA is commonly used solvent
- High corrosion, solvent degradation is concerned
- High energy consumption is also issue



◆ KS-1™ Solvent

- MHI R&D tested 200 solvents in pilot plant
- MHI developed proprietary KS-1™ solvent
- Process also optimized



2.2 Process Performance

- **Advantages of KS-1™ Solvent**

- ◆ **Low corrosive, corrosion inhibitor not required**

(Unit : mils (1/1000 inch) per year)

	Test 1	Test 2
MEA	93.0	76.4
MEA + inhibitor	9.5	8.3
KS-1™	3.1	3.6

Test condition : 130° C, in the presence of O₂

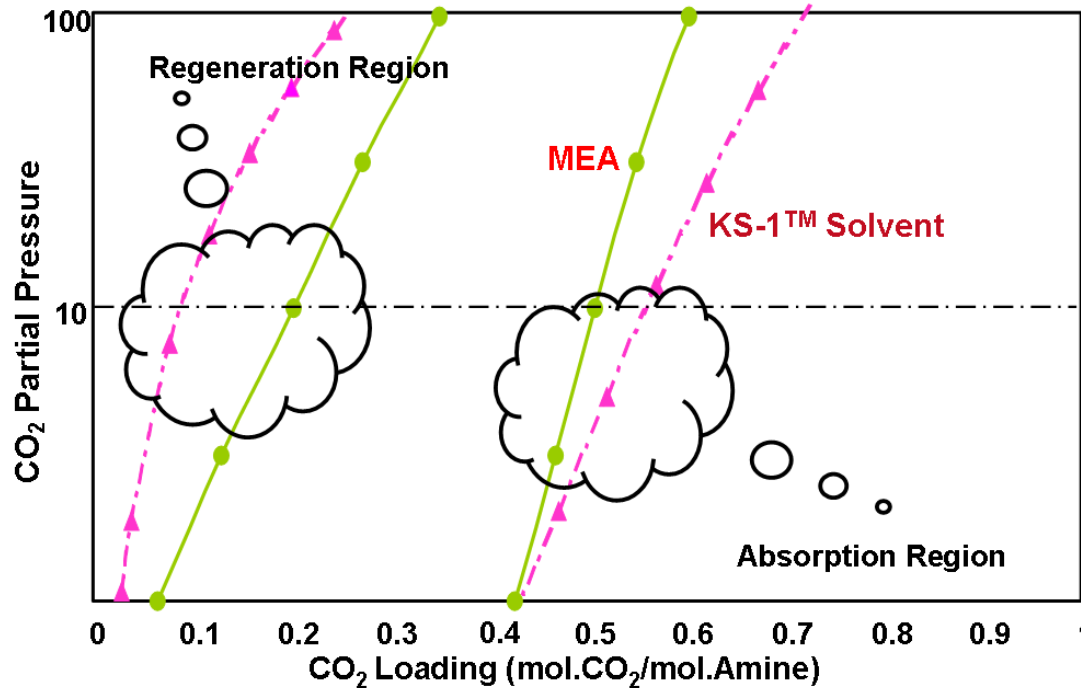
Corrosion test result



2.2 Process Performance

2.2.2 Utility Consumption

- ◆ **KS-1™ offers lower regeneration energy requirement**
- ◆ **MHI patented CDR process can reduce steam consumption by 30% compared to the conventional MEA process**

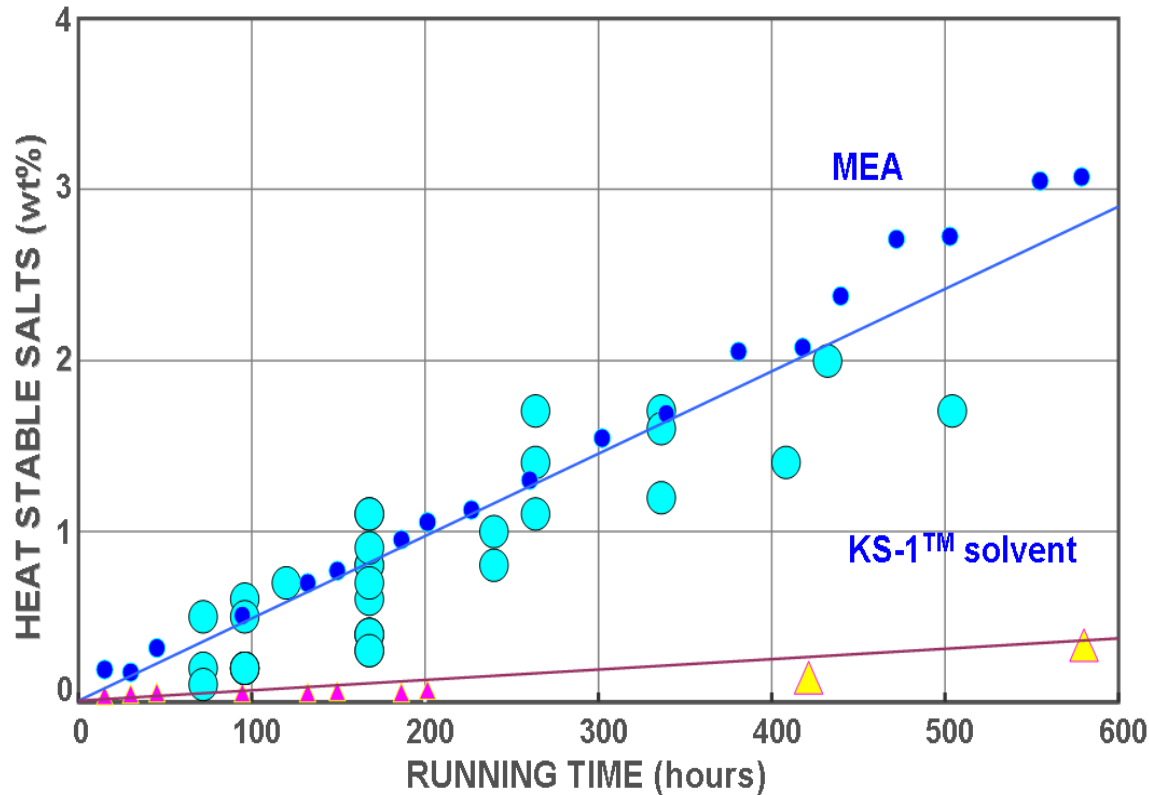


CO₂ Solubility KS-1™



2.2 Process Performance

◆ Low Degradation late



Heat Stable Salts (HSS)



2.2 Process Performance

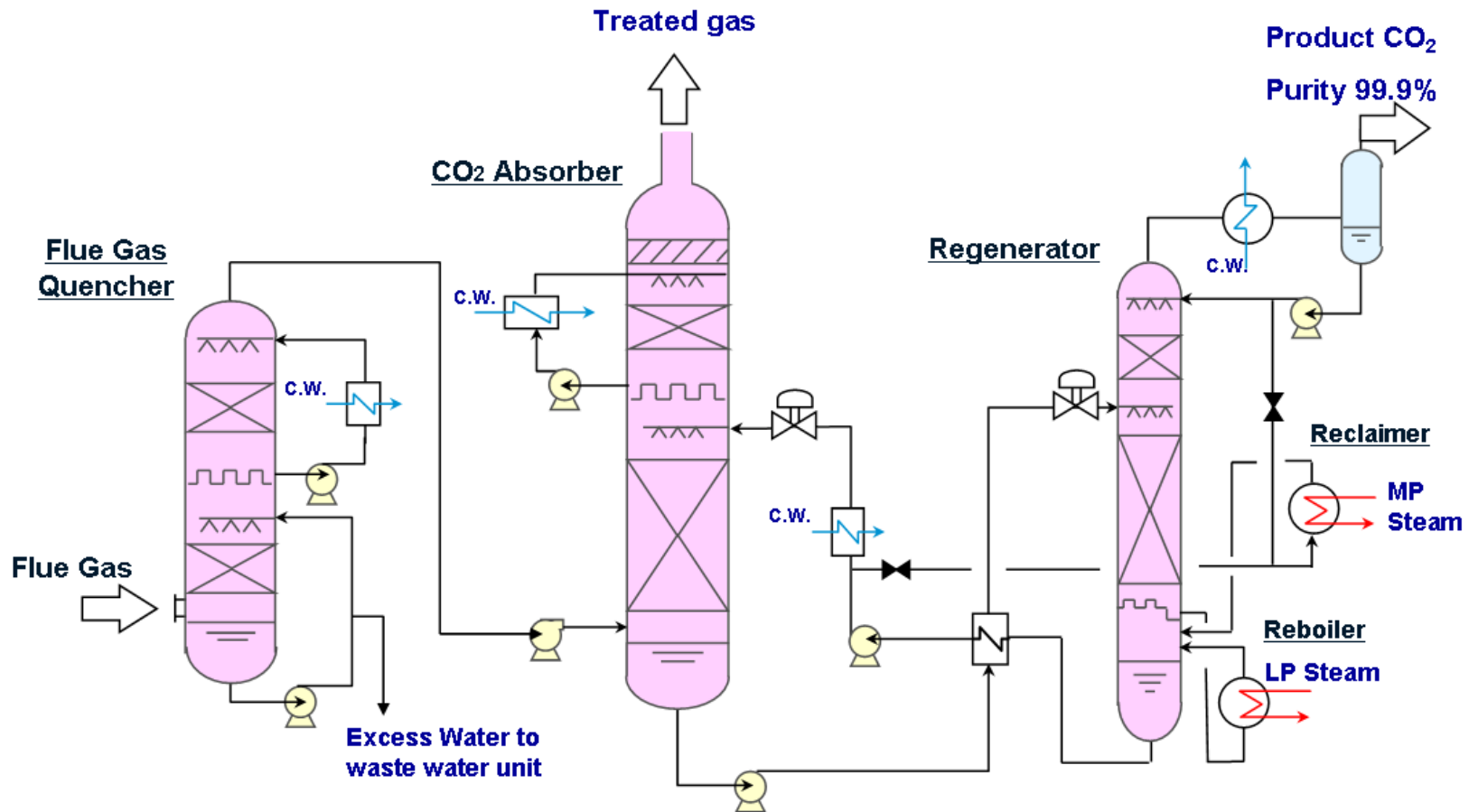
2.2.3 Operational Reliability

- ◆ **KM CDR Process™ based plants are highly available and reliable**
- ◆ **KS-1™ is very stable solvent**
- ◆ **It reduces frequency of reclaiming operation**
- ◆ **Reference plants experiences employed to improve the process and reliability**



2.2 Process Performance

2.2.4 MHI Post Combustion CDR Process



CO2 Recovery Process Flow



2.2 Process Performance

2.2.4 MHI Post Combustion CDR Process

- ◆ Main three sections,
 - The Flue Gas Quencher - To cool flue gas
 - The Absorber - Absorption and Washing
 - The Regenerator - Steam stripping of CO₂

- ◆ Water circulation in washing section

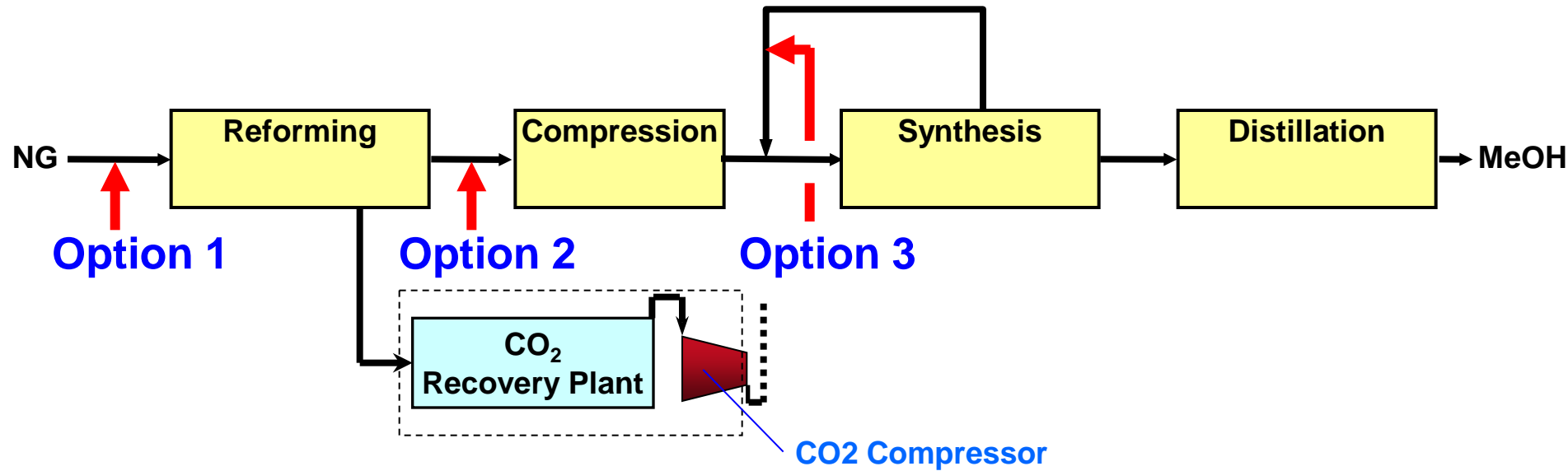
- ◆ Heat integration between Lean and Rich Solvent

- ◆ LP Steam used for stripping

- ◆ Stripped CO₂ with purity of 99.9% (Expected)



3. CO₂ Injection Point Enhancing Methanol Production



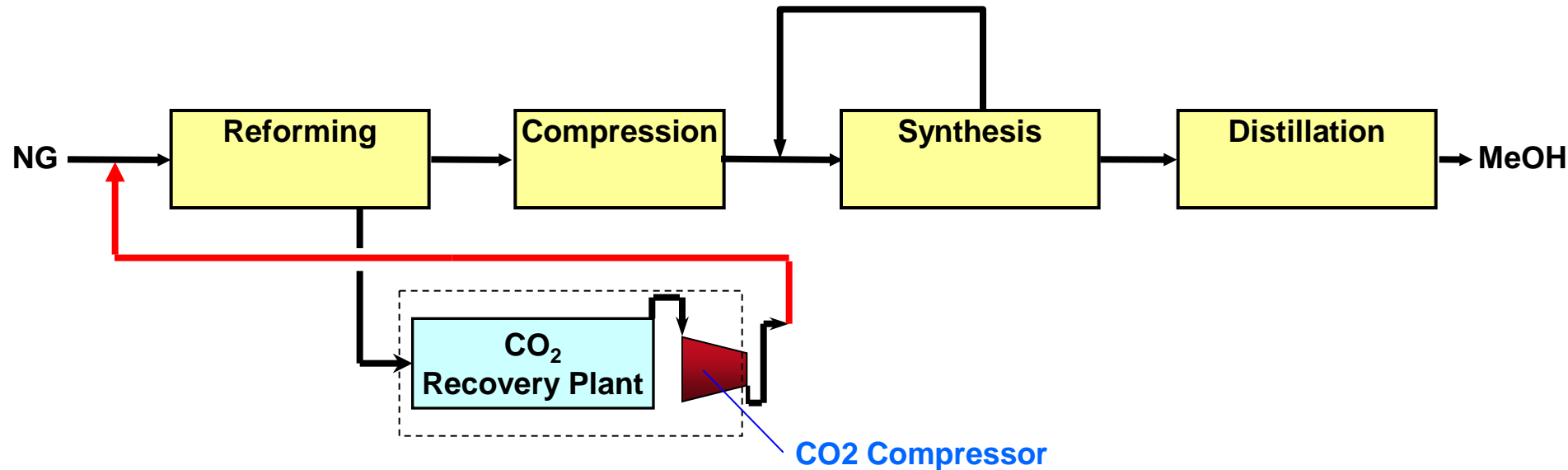
Option-1: Reformer Inlet

Option-2: Syn gas Compressor Inlet

Option-3: SynGas loop line

3. CO₂ Injection Point Enhancing Methanol Production

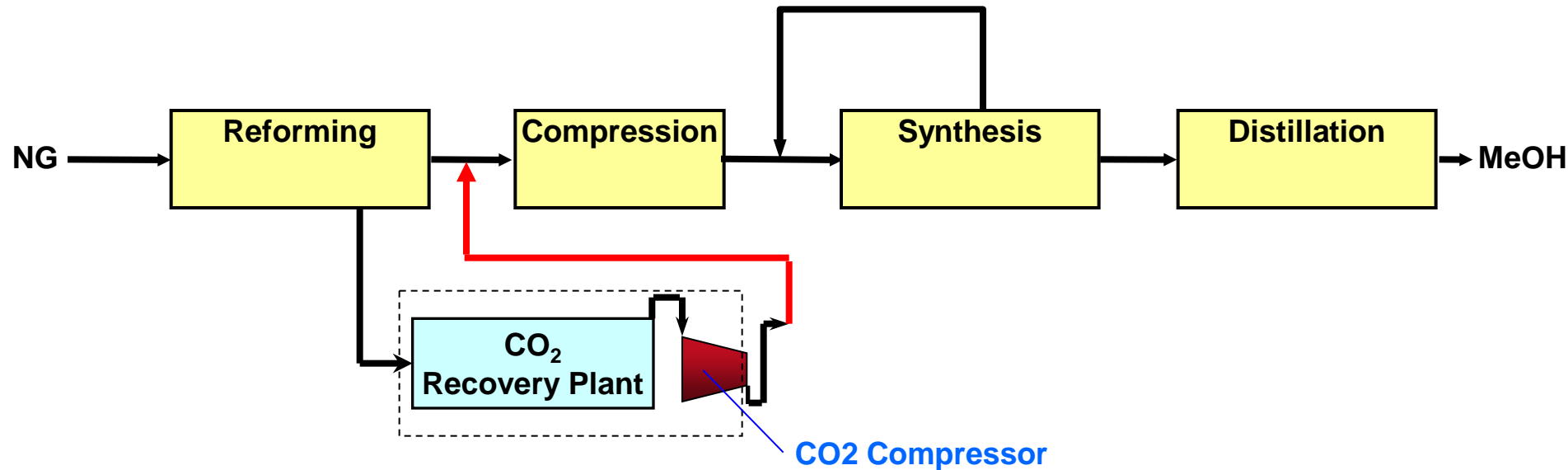
Option-1: CO₂ Injection at Reformer Inlet



- ◆ Part of CO₂ shifted to CO by reverse reaction
- ◆ Methanol synthesis from CO increase
- ◆ **Higher synthesis yield**
- ◆ **Capacity of Reformer and downstream system need to be debottlenecked**

3. CO₂ Injection Point Enhancing Methanol Production

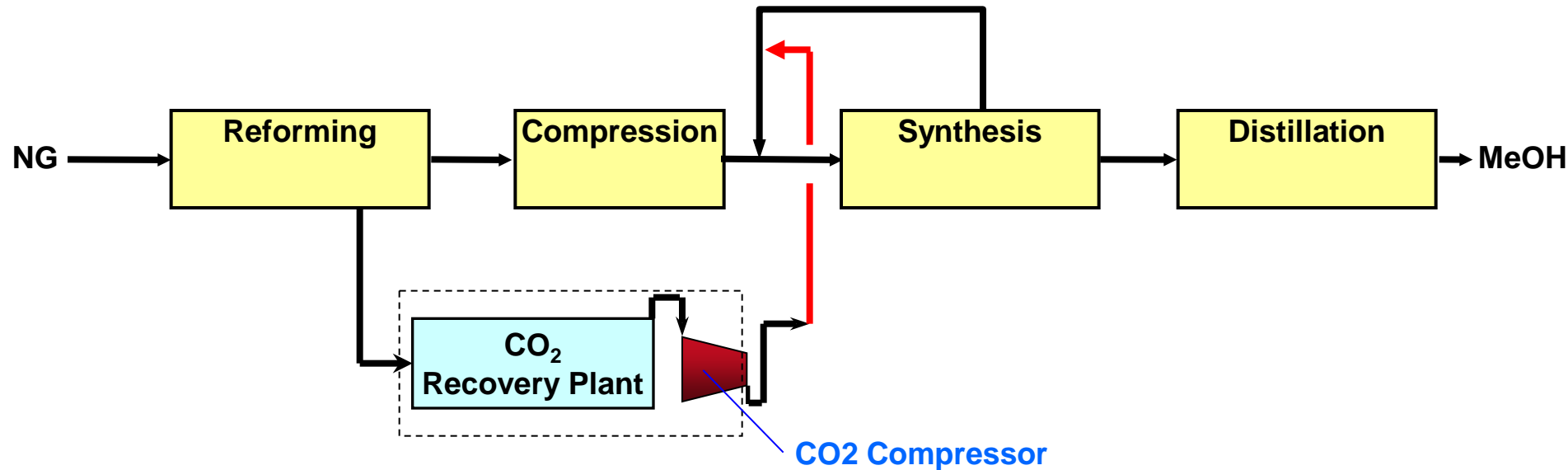
Option-2: CO₂ Injection at Syn gas Compressor Inlet



- ◆ Lower synthesis yield
- ◆ Capacity of SynGas compressor and downstream system need to be debottlenecked
- ◆ **Modification of reformer is not required**

3. CO₂ Injection Point Enhancing Methanol Production

Option-3: CO₂ Injection in SynGas loop line



- ◆ Lower synthesis yield
- ◆ CO₂ compressor required head is much higher than other cases
- ◆ Capacity of synthesis loop and all downstream have to be debottlenecked
- ◆ Modification of critical equipment such as reformer and Syn gas compressor is not required.

4. References for Methanol Production Enhancement

- ◆ **Location** : Qatar
- ◆ **Technology** : KM CDR Process™ by MHI
- ◆ **Contractor** : Mitsubishi Heavy Industries Engineering & Services Private Ltd. (MIES)
(100% Subsidiary Company of MHI established in Singapore)
- ◆ **Capacity** : 500 t/d
- ◆ **Source** : Flue Gas from Methanol Reformer
- ◆ **CO₂ Use** : Methanol Production Enhancement
- ◆ **Start-up** : 2014



5. Conclusion

- ◆ MHI has developed KM CDR Process™
- ◆ This process is applied to ten (10) commercial plants
- ◆ KM CDR Process™ and KS-1™ solvent are tried, tested and guaranteed
- ◆ Recovered CO₂ can be utilized to increase the methanol production capacity
- ◆ Recently MIES is engaged with 500 t/d capacity CDR plant for Methanol production enhancement



Thank You

