YMCE Engineering

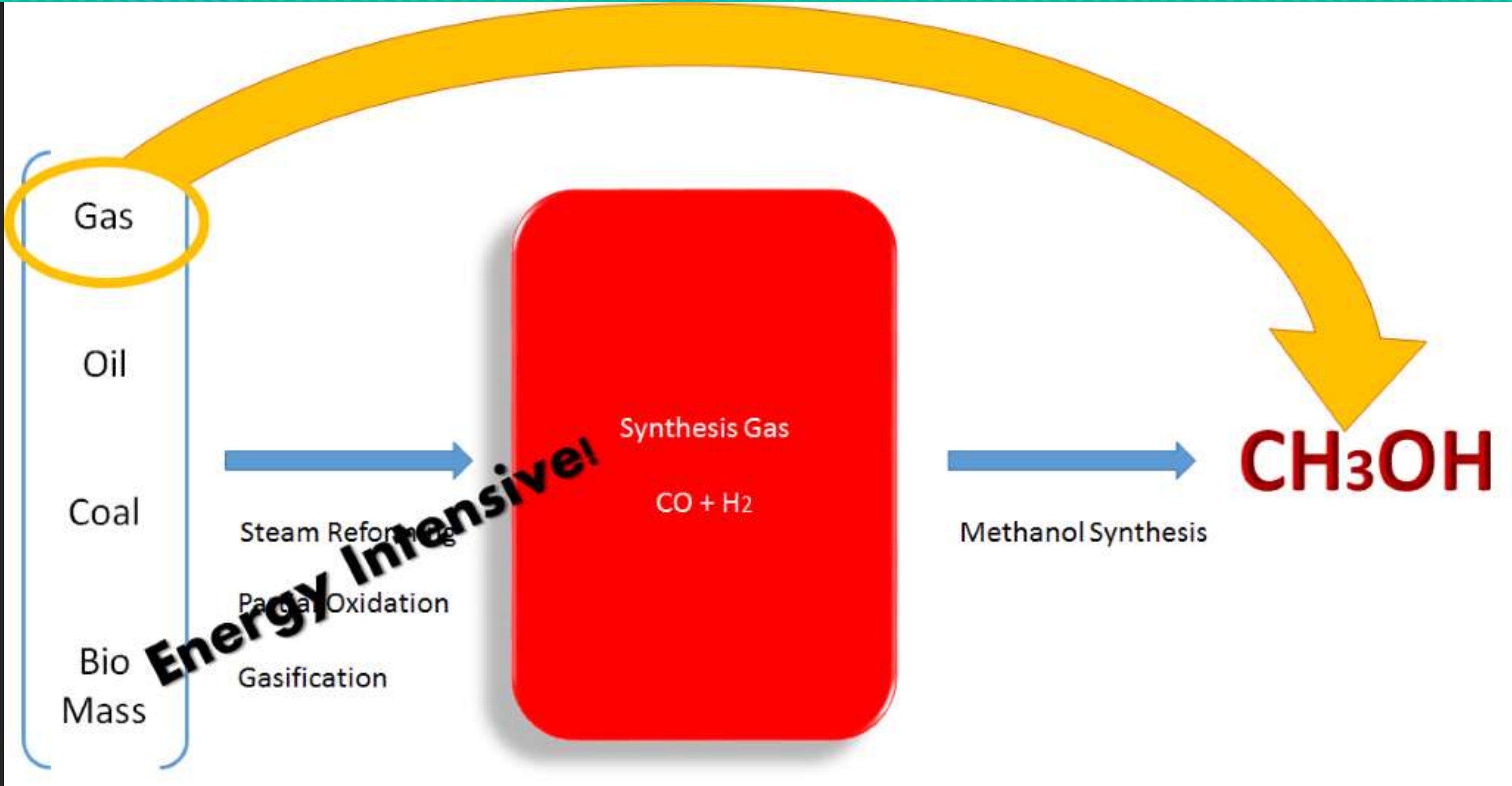
Direct Conversion of Methane to Methanol

Yousif Alqatari, Michael Seas, Christian Jones and Eric Fabrizius

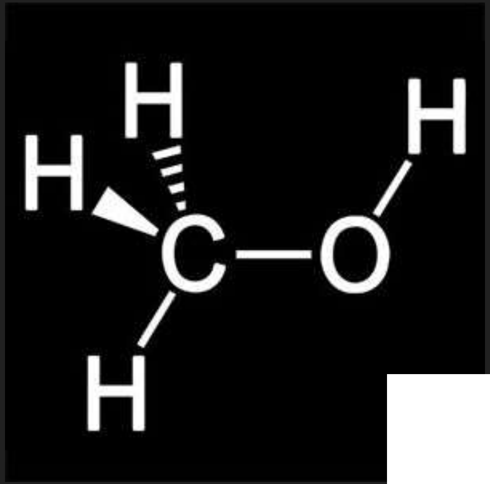
Introduction

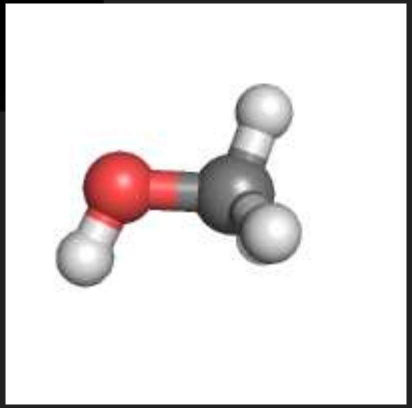
- Directly converting methane to methanol is necessary to conveniently transport natural gas from its production regions to consumption regions.
- 25% of the United States' energy production is currently derived from natural gas.
- Natural gas reserves are estimated to be 187.3 trillion cubic meters (55.7 years of global energy production)
- Production and use of natural gas are strongly limited by the difficulties in the transportation of the commodity.

Introduction



Business Opportunity



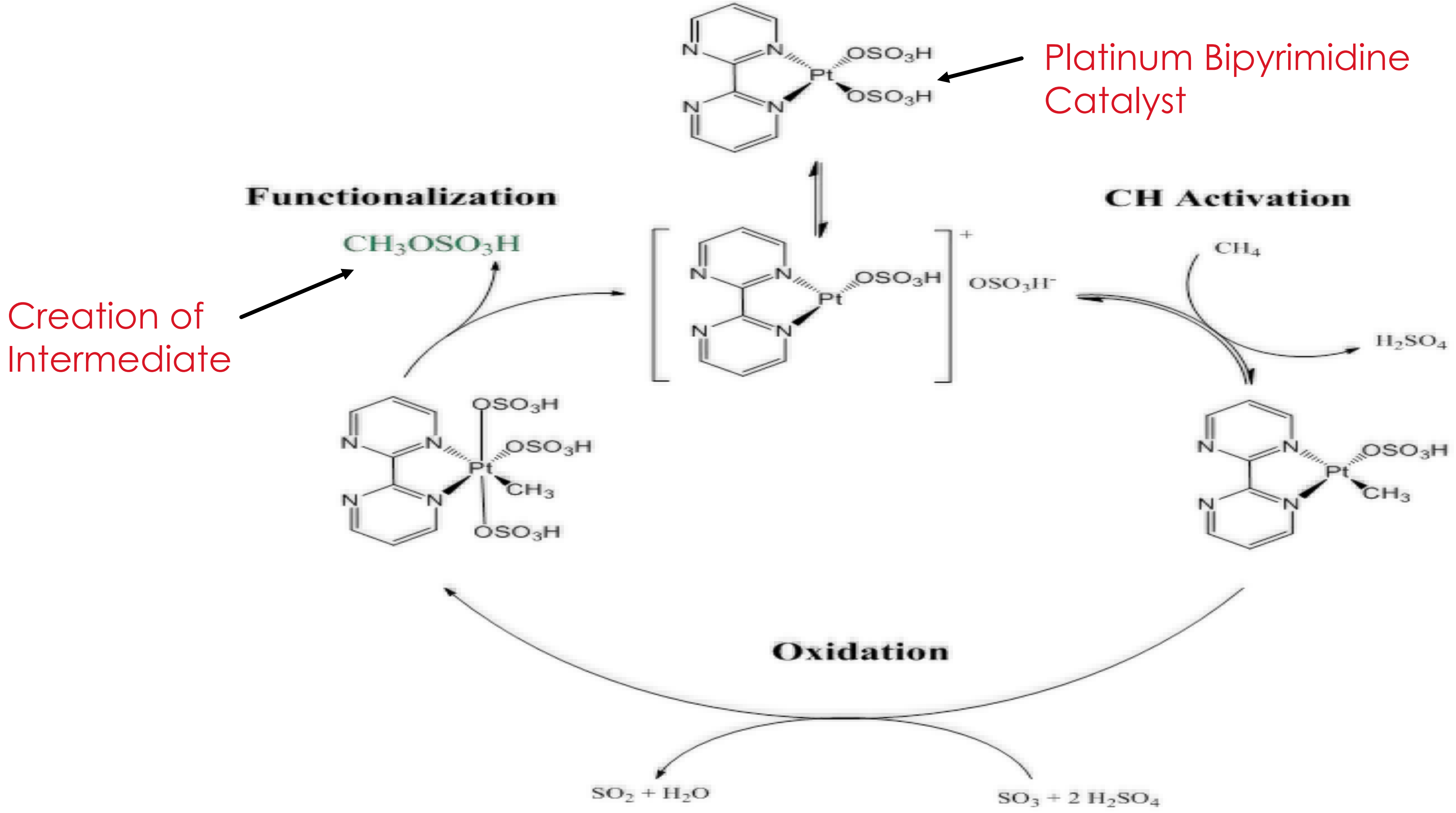


- Location: Houston, TX
- Methane is cheap. Methanol is very versatile compound
- In 2013, methanol global demand was about 65 million metric tons
- The global methanol industry generates $36 billion in economic activity each year, while creating over 100,000 jobs around globe.
- Sources of revenue: Methanol, Nitrogen from air separation unit.

Description of Base Case

- Platinum bipyrimidine catalyst is used to convert methane directly to methanol in the presence of fuming sulfuric acid and stoichiometric oxygen.
- Of the methane fed to the reactor:
  - 56% is converted to methanol
  - 22% is converted to combustion products (CO, CO_2)
  - Unconverted methane is recycled to the front of the reactor and purged at a 1:1 ratio
- Aspen Plus simulation is producing 99.9% methanol product
- 100% separation, recovery, and regeneration of the solvents (sulfur trioxide and sulfuric acid).

Reaction Pathway



Reaction Pathway

Intermediate shown in **GREEN**

Methanol Product shown in **BLUE**

Step 1 - Methane Activation

$$CH_4 + H_2SO_4 + SO_3 \longrightarrow CH_3OSO_3H + H_2O + SO_2$$

Step 2 - Intermediate Hydrolysis

$$CH_3OSO_3H + H_2O \longrightarrow CH_3OH + H_2SO_4$$

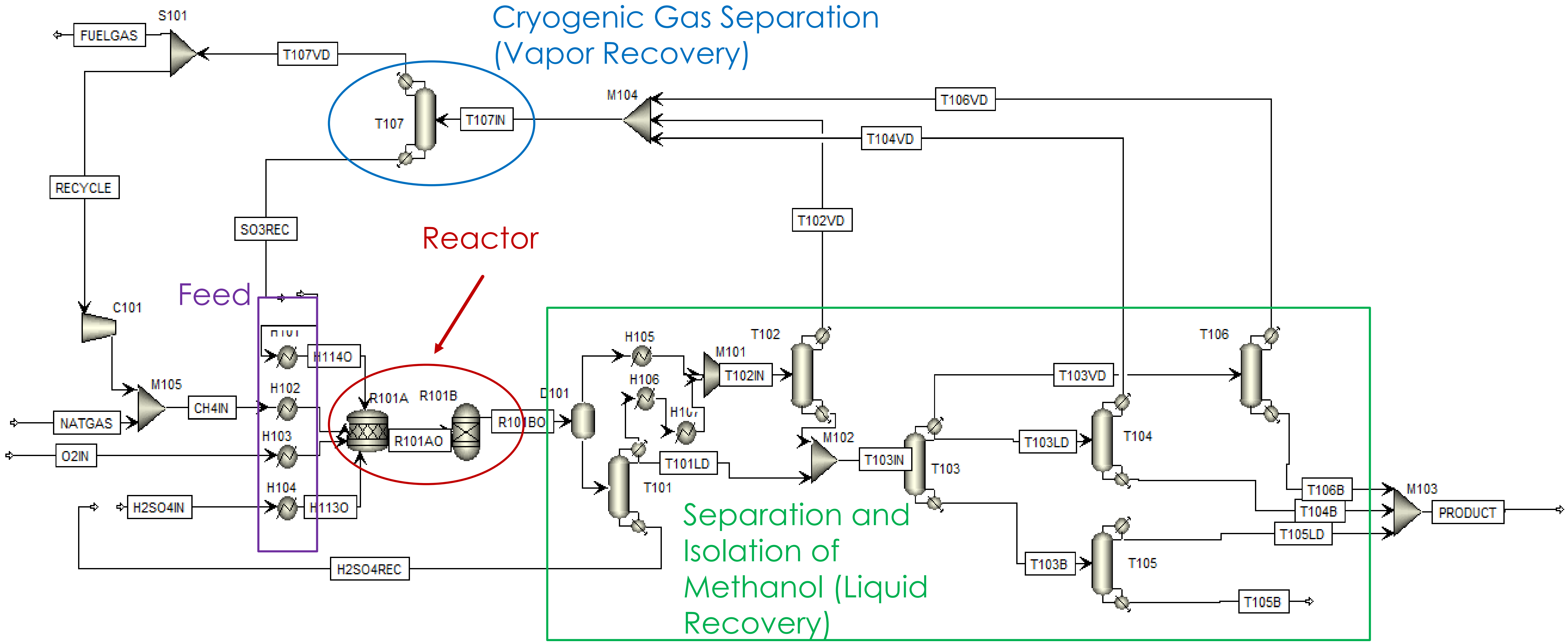
Step 3 - Catalyst Regeneration

$$SO_2 + 1/2\ O_2 \longrightarrow SO_3$$

Net Reaction

$$CH_4 + 1/2\ O_2 \longrightarrow CH_3OH$$

Description of Base Case



Feed

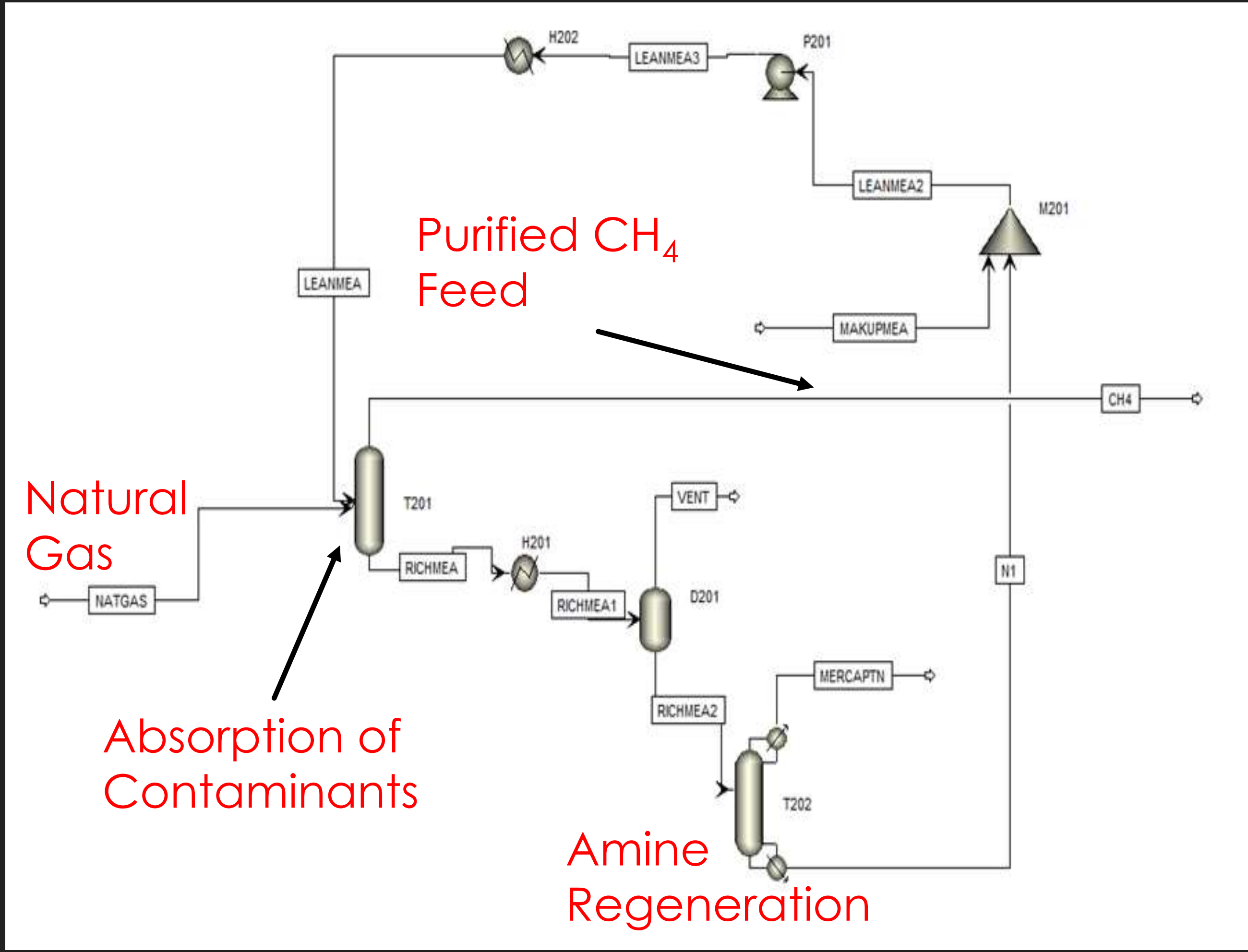
The feed flow to the reactor consists of four streams

1. Oxygen feed – from a cryogenic distillation unit (90% O_2 and 10% N_2)
2. Vapor recycle stream – containing recovered SO_3
3. Liquid recycle stream – recovered H_2SO_4 from acid distillation (as well as small amounts of water)
4. Methane feedstock – purified natural gas containing +98% of methane with some heavier hydrocarbons. Methane is recycled back to the reactor

Methane Purification

Amine Scrubbing Unit:

- Prevents catalyst deactivation
- Utilizes diisopropylamine to remove the methyl mercaptan from the methane feedstock
- Produces 98.5% pure methane
- 1.5% of the feed is higher carbon gases
- Trace amounts of sulfur in methane feedstock



Reactor Description

- Reactor Type-

  Continuous Stirred Tank Reactor (CSTR)
- Volume: 3000 ft^3(≈ 22,000 gal)
- Pressure: 600 psia
- Temperature 200°C
- Material: Hastelloy

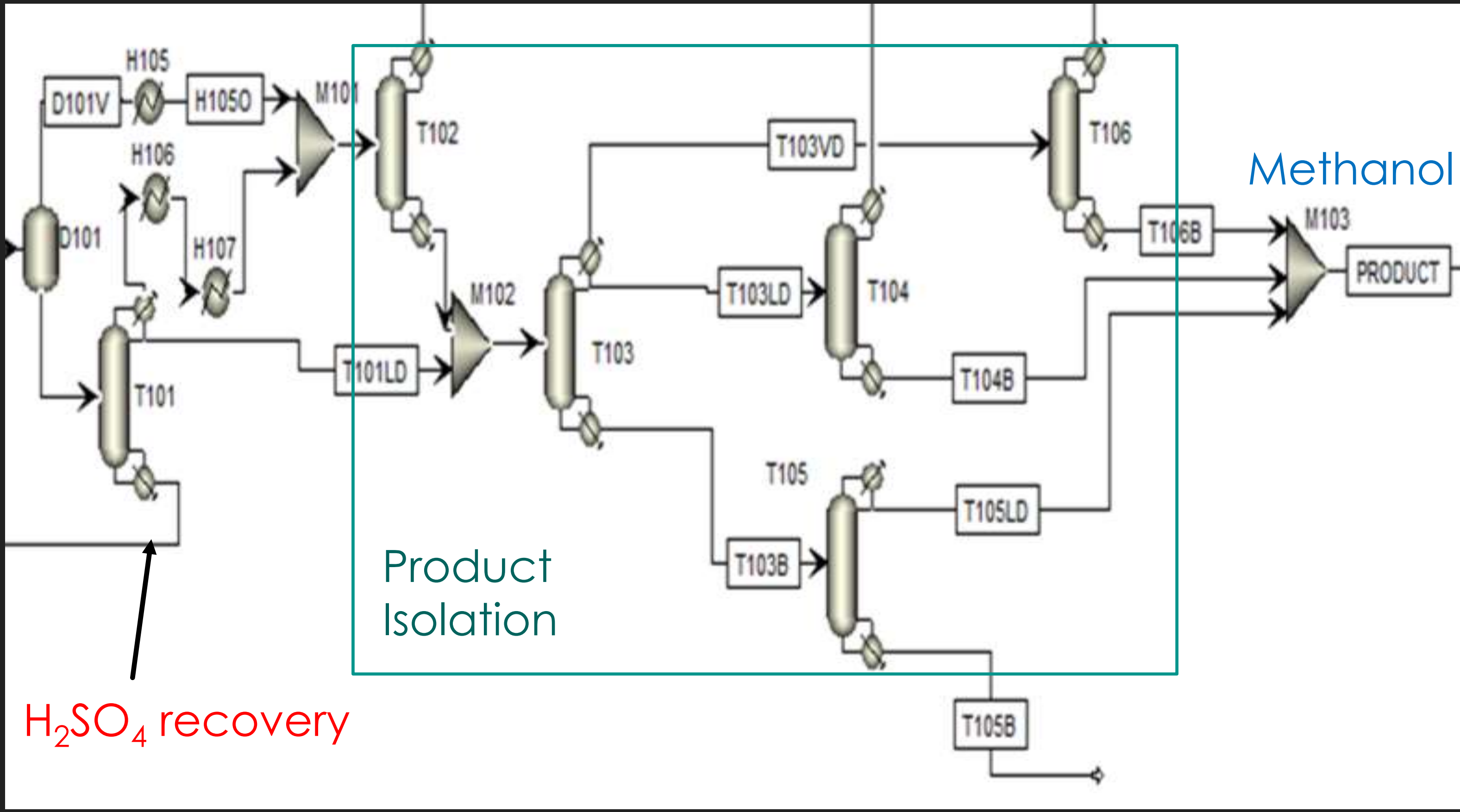
Reactor Effluent

Consists of a number of components:

- Sulfuric acid regenerated in catalytic cycle
- Water
- SO_3 regenerated from cycle
- CO/CO_2/various other hydrocarbon gases (i.e. $C_2 – C_4$)
- Unreacted Methane

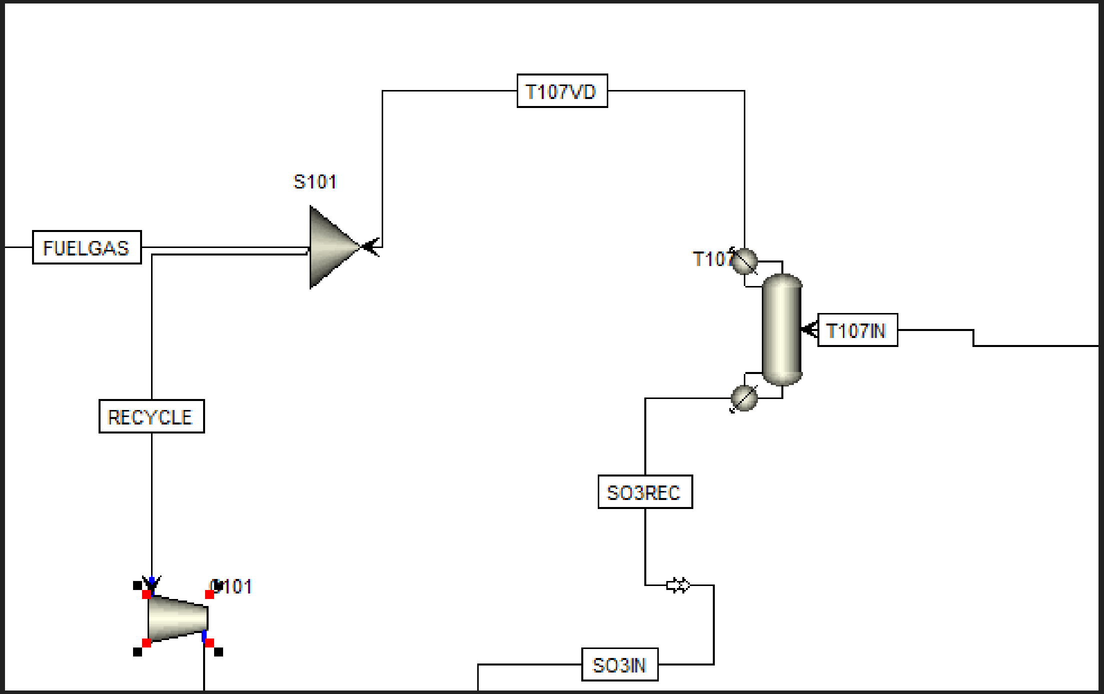
Dehydration and Isolation of Methanol

- Series of distillation towers and flash vessels separate gaseous components from liquid components
- Sulfuric acid is distilled first to reduce corrosion (recycled back to reactor)
- Methanol is dehydrated of its water component
- Methanol is produced at 99.9% purity

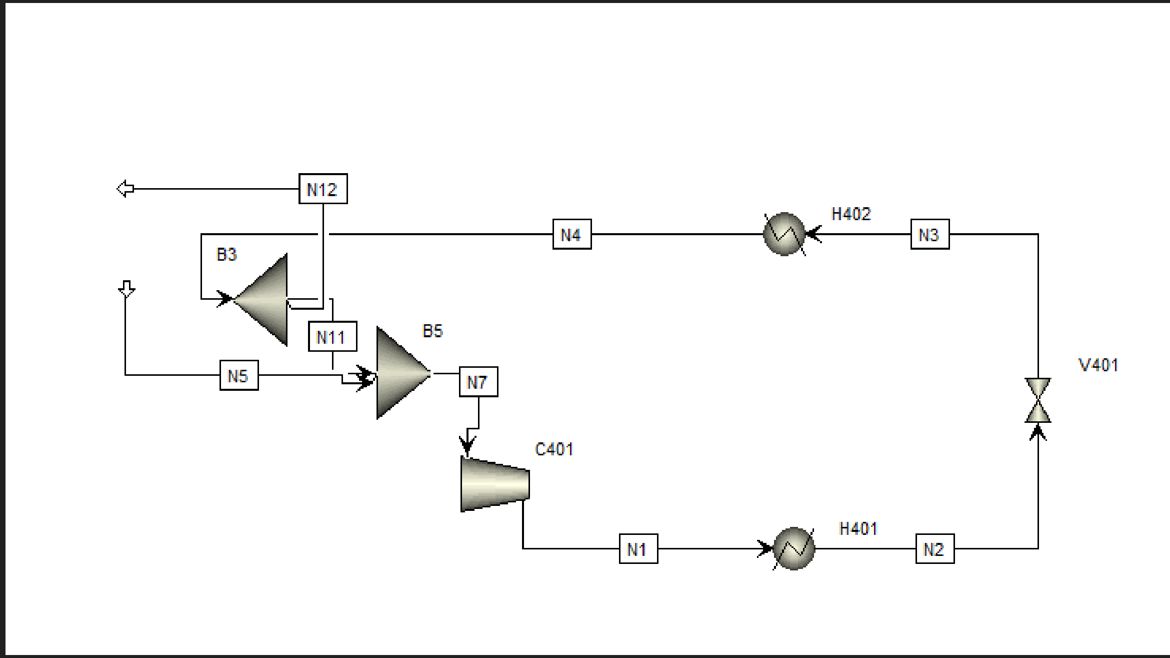


Cryogenic Distillation

- Used to separate SO_3 from other gaseous components in system



- Due to difference in nearest component boiling point 100% separation of SO_3 is achieved



Design Alternatives

1. Initial process design did not include catalyst (Partial Oxidation of Methane)
   - Reactor Operating Conditions:
     - 7% conversion, 76% selectivity, 750K, 735psi
2. Current process design utilizes homogeneous platinum catalyst
   - Reactor Operating Conditions:
     - 56% conversion, 78% selectivity, 473K, 600psi
3. Potential future process design may use heterogeneous *Co/ZSM-5 zeolites* catalyst
   - Reactor Operating Conditions:
     - 18% conversion, 50% selectivity, 423K

Design Alternatives

Partial Oxidation Alternative:

- Literature and Aspen Plus simulation work suggests that low conversion makes this route improbable
- Low conversion causes recycle stream of methane to be large
- Purge of recycle loses 20-40% of unreacted methane

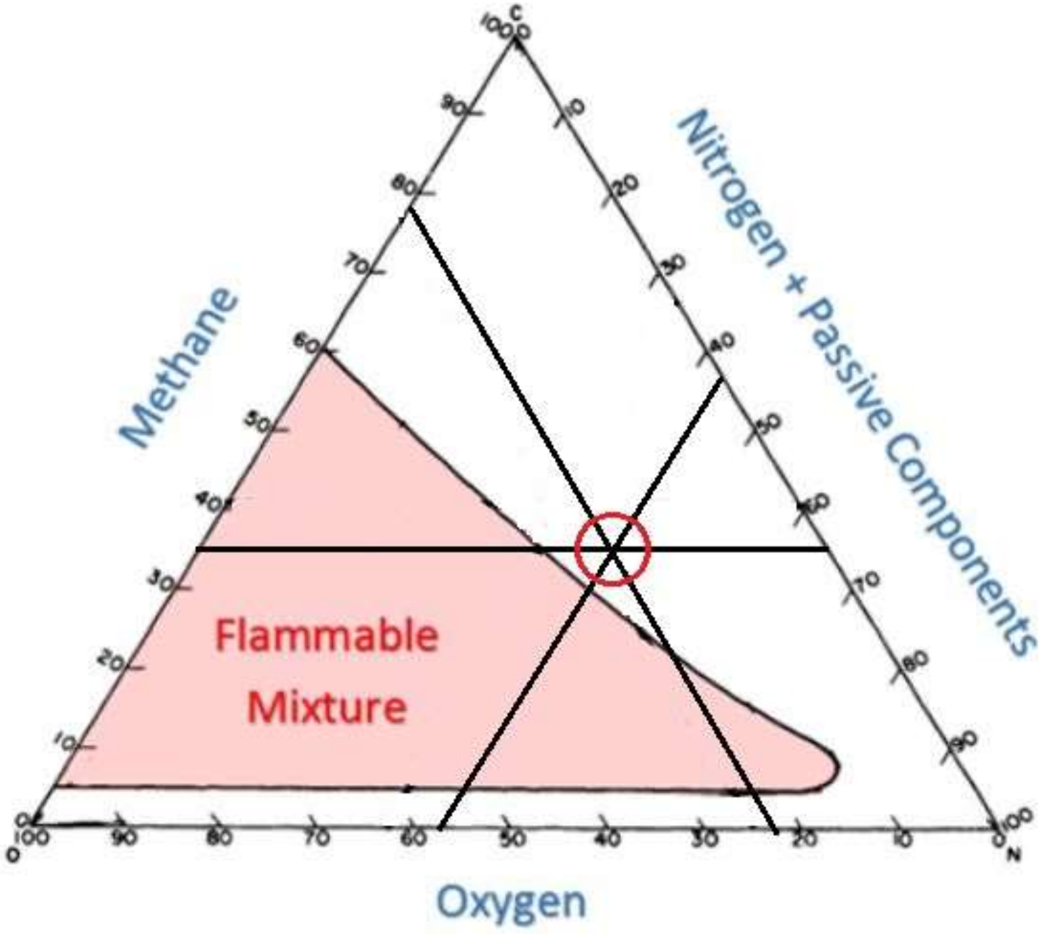
Heterogeneous Catalyst route:

- Low conversion and selectivity, which creates issues similar to those described above
- Less methane loss in purge, but greater separation of reactor effluent needed

Safety and Risk Management

Reactor Composition (Vol %):

Methane 34%
Oxygen 25%
Nitrogen + Passive Components 42%



Safety and Risk Management

- Rupture disk to counter possible reactor ignition
- Reactor rated for high pressure
- Exotic reactor material

Project Economics

Summary of Base Case Parameters

Case	ISBL (MM$)	FCI (MM$)	Residence Time (hr)	Catalyst Cost ($/lb)	Material Multiplier
Base	$55.9	$61.5	2.5	100	4

Catalyst Rebuy Period (years)	Methane Price (c/lb)	Methanol Price (c/lb)	Operating Time (hrs)	NPV15 (MM$)	IRR %
10	6.04	15	8640	60.12	15.60%

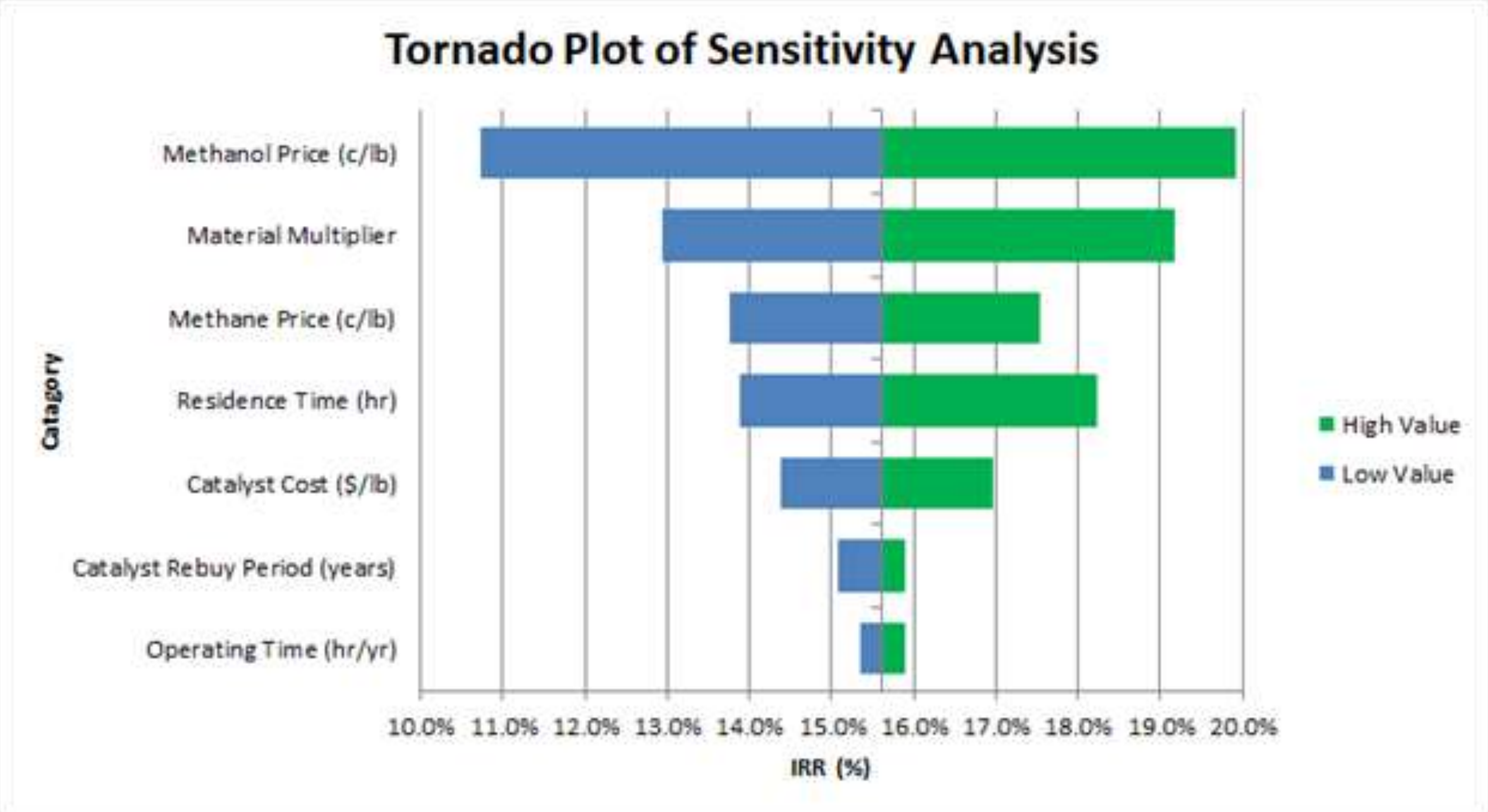
Major Equipment Costs

Equipment	ISBL FOB Cost ($)	Percentage of Total ISBL
Air Seperation Unit	$ 860,000	8%
Compressor	$ 1,800,000	17%
Heat Exchangers	$ 2,057,387	20%
Reactor	$ 144,913	1%
Vessels	$ 394,990	4%
Towers & Trays	$ 5,064,271	49%
TOTAL ISBL FOB	$ 10,321,562	100%

Installation Factor	504%
Installed ISBL	$ 55,922,223
Installed OSBL (10% of ISBL)	$ 5,592,222

Installed FCI	$ 61,514,445

Project Economics



Environmental

	Total Emission (ton/yr)
CO_2	5919
SO_x	75
NO_x	0.00438

- New Source Review, Building Permits and Hazardous Waste Permit needed before construction begins

- Emission of priority pollutants, SOx and NOx, are below 100 ton per year limit
- In the event of increase in emissions
  - Low NOx Burner for NOx emission
  - Limestone scrubbers for SOx emission
- Greenhouse gas regulations will require control of CO_2 emission
  - Carbon capture and sequestration is a known control strategy

Local/ Global Impacts

- Local:
  - Employment opportunities
  - Attract businesses using methanol as feedstock/building block: Acetic acid, formaldehyde, etc.

- Global:
  - Transportation industry: superior vehicle performance when compared to gasoline. Less toxic emissions.
  - Electricity generation: used to drive turbines to create electricity
  - Wastewater denitrification

Conclusion/ Recommendations

- Limited amount of scale up information available
- Validation of process chemistry is necessary
- Environmental issues with very corrosive solvent
- Further development of heterogeneous catalyst
  - Process safer than homogeneous catalyst
  - Easier recovery of heterogeneous catalyst

Questions