

# METHANOL PURIFICATION SYSTEM

Allan Jensen, Ph.D, P.Eng, Technical Manager, A.H. Lundberg Systems Limited, Vancouver, B.C., Canada

Trevor Ip, P.Eng, Project Manager, Alberta Pacific Forest Products, Boyle, Alberta, Canada

Jamie Percy, B.Sc (Eng), Process Engineer, Alberta Pacific Forest Products, Boyle, Alberta, Canada

## ABSTRACT

Methanol is formed as a by-product of the kraft pulping process. Due to its high relative volatility to water, a large fraction of this methanol will be present in the vapour phase and therefore can be captured in a relatively small foul condensate stream. Many kraft facilities, including the Alberta Pacific Forest Industries (Al-Pac) mill, operate a foul condensate steam stripping system, producing methanol rich stripper off gas (SOG).

At Al-Pac, SOG is currently disposed of through incineration in the lime kiln or power boiler; this flow is to be diverted to the new methanol purification system designed and supplied by A.H. Lundberg Systems Limited. The methanol is recovered by separating it from water and other contaminants through distillation, producing a methanol product at a minimum of 99.85wt% purity. Some of the purified methanol is to be used internally for the production of chlorine dioxide with the balance for external sale.

## INTRODUCTION

### Process Overview

The methanol purification system is based on the unit operation of distillation (see Figure 1). The system includes two distillation stages. In the first “topping” stage, the compounds more volatile than methanol, such as  $H_2S$  and ammonia, are removed in the vapour phase while the methanol, water and other less volatile compounds remain in the bottoms. In the second “rectification” stage, the purified methanol is recovered from near the top of the column while the water and other less volatile compounds are removed in the bottoms.

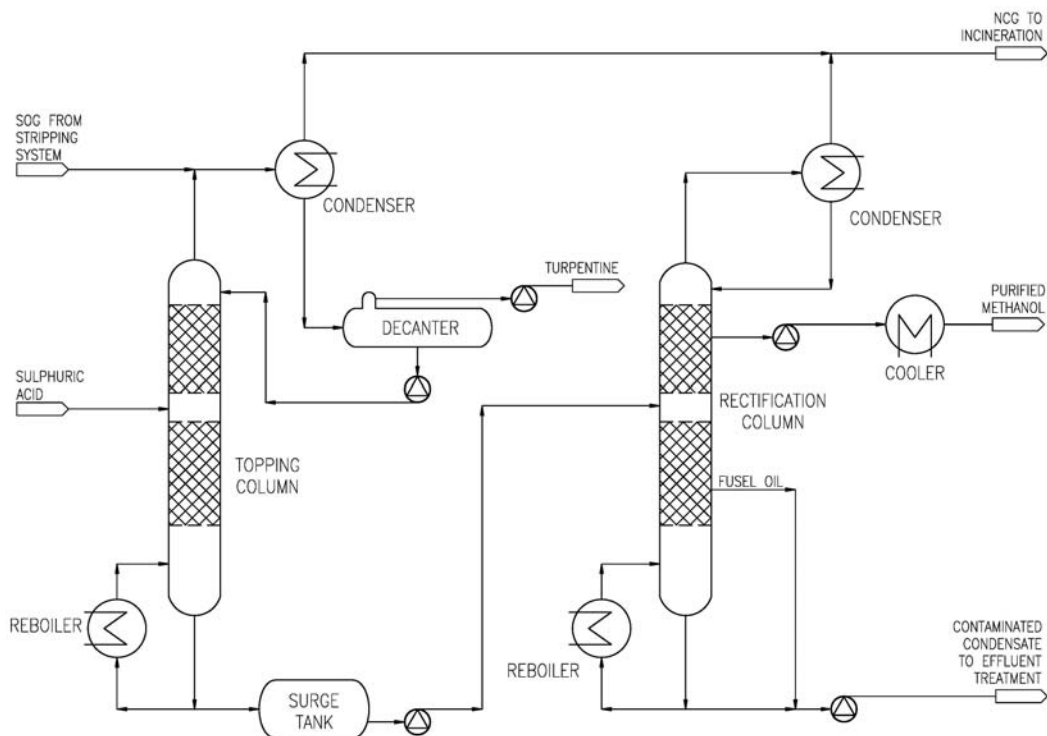


Figure 1: Methanol Purification System Process Flow Diagram

There are numerous methanol purification systems in operation around the world and their operation is well understood, but this process had not previously been applied to this feed stream. Recovery of methanol from kraft pulping condensates has several unique characteristics that inhibit separation by distillation:

- Azeotropes of methanol and organic contaminants
- Immiscibility of terpenes
- Dissociation of hydrogen sulphide and methyl mercaptan
- Ammonia reacting to produce ammonium sulphate (fouling)

A.H. Lundberg has developed and patented features to deal with each of these design issues [1].

### Modular Construction

The Methanol Purification System was supplied in modular form (see Figure 2). All equipment, inter-connecting piping, handvalves, instruments, control valves, and insulation were supplied pre-assembled on steel skids.



**Figure 2: Methanol Purification System Module**

### PROCESS DESCRIPTION

The presence of azeotropes between methanol and some organic contaminants require that the SOG generated in the stripping system be no higher than 40wt% methanol to ensure separation of the contaminants in the topping system. SOG is introduced to the methanol purification system at a stable concentration and at a controlled flow, with the balance continuing on through to the incineration point. The purification system is designed to process all of the SOG flow, but effective distillation requires stable operation including consistent SOG feed flow and quality. In some cases, this requirement will necessitate upgrading the stripping system.

## Stripping System Upgrade

Many existing stripping systems, including the Al-Pac system, utilize a reflux condenser integrated with the multiple effect black liquor evaporator plant. In this arrangement, control of the stripping system is compromised because any upsets in evaporator operation will cause an upset in the stripping system and a subsequent swing in SOG quantity and concentration. The Al-Pac stripping system was de-coupled from the evaporator set with installation of a dedicated reflux condenser. The steam energy added to the stripping system is recovered by heating demineralized boiler feed water in the condenser. Installation of this condenser had several side benefits including a reduction in overall steam consumption and the ability to operate the stripping system when the evaporator plant is down.

## Topping System

SOG is composed mainly of methanol and water vapour, but it also contains over 150 different organic “impurities” including various aliphatic alcohols and ketones, terpenes, along with sulphur and nitrogen compounds [2]. The topping column is designed to strip out the “low boilers” and noncondensibles from the SOG, including the odorous TRS compounds, ammonia, and some ethers, ketones, and aldehydes.

SOG is combined with the vapour from the topping column and introduced to the topping reflux condenser; the low boilers and noncondensibles are vented back to the SOG incineration system while the reflux condensate is drained to the red oils (turpentine) decanter. Heat is added to the topping column via a steam reboiler with this heat recovered into demineralized water in the topping reflux condenser.

Contaminants produced during the kraft pulping of wood include the ionizable sulphur compounds, hydrogen sulphide and methyl mercaptan. The removal of these compounds by distillation is directly related to the pH of the liquid phase in the column. For example, at a pH above about 6, hydrogen sulphide begins to dissociate, and at a pH above about 9, this occurs with methyl mercaptan (see Figure 3). In their dissociated form, these compounds do not exert a vapour pressure and therefore cannot be removed by distillation.

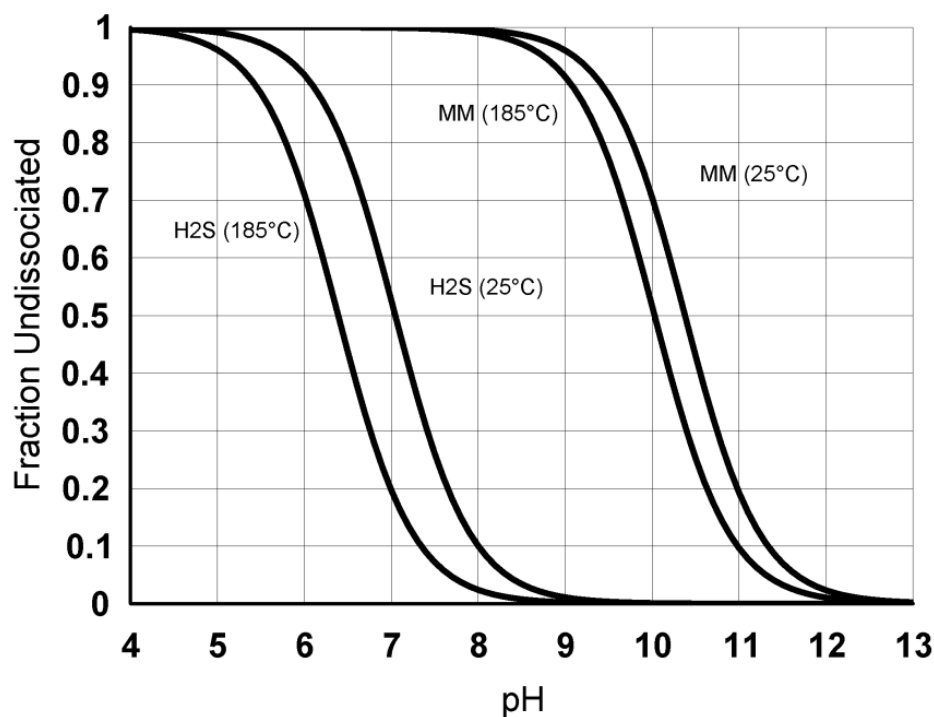


Figure 3: Dissociation of Hydrogen Sulphide and Methyl Mercaptan

The pH of condensed SOG is typically slightly alkaline at about 8 to 9. To ensure that ionizable sulphur compounds are removed, sulphuric acid is added to the topping column. Due to the presence of ammonia, the acid cannot simply be added to the liquid feed to the column as it will react with ammonia producing ammonium sulphate.

Ammonium sulphate is very soluble in water (about 0.7 kg dissolved per kg water at 25°C and 1.0 kg per kg at 100°C), but completely insoluble in methanol. Unfortunately there is no data available for solubility in water/methanol mixtures but it likely at best only partly soluble. To ensure that no ammonium sulphate forms, potentially fouling the topping column, the sulphuric acid is added at the mid-point of the column; the top section of the column is therefore used to strip out the highly volatile ammonia before it has a chance to react with the acid.

Sufficient acid will be added to lower the pH to between 5 and 6, thereby releasing the newly undissociated hydrogen sulphide and methyl mercaptan. These are stripped out in the bottom section and then must rise up through the top section of the column. These gases, when reabsorbed, are weak acids and will cause a slight decrease in the pH in the top section of the column, but no ammonium sulphate precipitate will form due to lack of any sulphate ions in solution.

### **Red Oils Decanting**

Terpenes, naturally present in wood, are extracted during kraft pulping, and due to their extremely high relative volatility, will collect in the foul condensate. Those not decanted in the turpentine recovery system will make their way to the stripping system and subsequently into the SOG. The mixture of terpene compounds is also referred to as turpentine, or crude sulphate turpentine, or, when heavily contaminated with TRS compounds, "red oils", due to their distinctive red hue. The terpenes are almost totally immiscible in the methanol solution; therefore a red oils decanter is required. The decanted red oils are pumped to the turpentine recovery system. At Al-Pac, the turpentine is disposed of through incineration. If the turpentine is to be sold, the red oils should be processed separately as their high TRS content will degrade the quality of regular turpentine.

### **Surge Tank**

The underflow from the topping column flows by gravity to the surge tank. This tank is sized for about 90 minutes of retention; therefore, it provides operational flexibility by separating the topping system and rectification system processes. The tank also provides volume to homogenize the methanol solution feed flow to rectification.

### **Rectification System**

The methanol solution from the surge tank is pumped to the rectification column, and flows down through the stripping section countercurrent to the stripping steam, thereby driving off the volatile constituent (methanol) to be removed from the less volatile (water, ethanol, etc). This column is designed to separate the water and other "high boilers" into the underflow, and methanol vapour into the overhead vapour flow. Heat is added to the rectification column via a steam reboiler.

"Intermediate boilers," such as some higher alcohols (primarily ethanol) and higher ketones are drawn off from the bottoms column below the methanol solution introduction point; these are referred to as "fusel oils." They are combined with the underflow from the column, but can in future be recovered separately if desired. Typically a fusel oil flow sacrificing about 2 to 3% of the methanol must be bled off to ensure that the methanol product remains free of ethanol contamination. The contaminated condensate from the rectification column is pumped away to effluent treatment.

The vapour from the top of the stripping section passes up to the rectification section. Vapour from the top of the column is condensed in the rectification reflux condenser, with low boilers and noncondensables (not removed in the topping column) vented back to the SOG incineration system. The heat introduced by the reboiler steam is recovered into demineralized water in the rectification reflux condenser. The reflux condensate is pumped back to the rectification column.

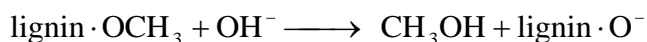
## Methanol Product

The 99.85+ wt% methanol product is drawn off slightly below the top of the packing. The methanol is drawn off in sufficient quantities to maintain the temperature (and therefore methanol concentration) profile in the column. The methanol is pumped via the methanol cooler to a new storage tank. If necessary, the methanol product can also be recycled back to the surge tank, recycled back to the stripper feed tank, or fired in the lime kiln via the turpentine lance.

## METHANOL RECOVERY AND USAGE

### Methanol Formation

Methanol is formed as a by-product of the kraft pulping process; in the digester, the hydroxyl ion reacts with a lignin methoxyl group:



The amount of methanol produced is dependent on:

- Wood species: in general lignin methoxyl groups are more numerous in hardwoods than softwoods therefore more methanol is formed.
- Hydroxyl concentration: higher alkali charge will produce more methanol.
- Temperature: higher cooking temperatures will produce more methanol.
- Time: longer cooking times will produce more methanol.

Some methanol is also formed from the acid-catalyzed methanol elimination from hemi-cellulose, while naturally occurring methanol is freed from the biomass at the start of pulping.

In Table 1, Zhu, et al. provide estimates for methanol formation when producing bleachable grade kraft pulp from various softwoods and hardwoods [3].

**Table 1: Methanol Formation in Kraft Pulping**

Wood Species	Methanol Formation (kg/ODT Pulp)
Western Hemlock	7.3
Douglas Fir	8.3
White Spruce	9.1
Southern Pine	9.3
Aspen	9.6
Birch	11.0
Maple	11.3
Oak	12.8
Bass	13.1
Sweetgum	15.0

## **Methanol Capture**

In a continuous mill, the methanol leaves the digester with the extraction liquor or with the brown stock. Methanol is relatively volatile compared to water, therefore a large fraction will tend to flash-off in the extraction liquor flash tanks, ending up in the digester foul condensate; smaller fractions will remain in the liquor or will be carried away by the Concentrated Noncondensable Gas (CNCG) collection system. Some methanol will also be lost to the Dilute NonCondensable Gas (DNCG) system during brown stock washing.

The methanol that is captured in the washing filtrate or that remains with the extraction liquor will eventually end up in the weak black liquor feed to the evaporators. Depending on the level of condensate segregation, anywhere from 50 to 90% of the methanol in the weak liquor will typically be captured in the evaporator foul condensate, with the remainder lost to the combined condensate and the CNCG vent. In a well operated stripping system, up to 95% of the methanol will be removed from the foul condensate and captured in the SOG, with 90% of this recovered as purified methanol. Overall, about 70 to 80% of the methanol formed in the digester is expected to be recovered as purified methanol.

## **Methanol Production**

Al-Pac is the largest single-line bleached kraft pulp mill in North America, running campaigns of about 85% Aspen and 15% Spruce and Pine, producing over 600,000 ADMT per year. The new methanol purification process is expected to produce about 3700 t/year of commercial grade methanol.

## **Commercial Grade Methanol**

A market study prepared for Al-Pac, showed that commercial grade methanol is currently produced from natural gas in countries, such as Chile, which are a significant distance from Canadian users. In 2006, global and Albertan methanol consumptions were 35 million and 360,000 tonnes per year, respectively. Methanol is used in the production of formaldehyde, methyl tertiary-butyl ether (MTBE), and acetic acid. It is also used in the transportation of natural gas by pipeline, as a fuel, and as a solvent [4].

The general standard observed by industry for methanol product purity is either U.S. Federal Specification O-M-232L Grade AA [5] or International Methanol Producers & Consumers Association (IMPCA) standards [6]; these are listed in Table 2.

Odour is a primary concern with kraft mill by-products, with reduced sulphur compounds the primary culprit. Grade AA simply states that the product should have “characteristic, non-residual” odour, whereas the IMPCA standard includes a sulphur maximum of 0.5 mg/kg.

**Table 2: Commercial Grade Methanol Specifications**

Component	Grade AA	IMPCA
Methanol content, wt%	> 99.85	> 99.85
Water content, wt%	< 0.10	< 0.10
Ethanol, mg/kg	< 10	< 50
Acetone, mg/kg	< 20	< 30
Total acetone and aldehyde, mg/kg	< 30	
Acid (as acetic acid), mg/kg	< 30	< 30
Colour index (APHA)	< 5	< 5
Sulphuric acid test (APHA)	< 30	< 30
Boiling point range, I °C	< 1	< 1
Dry residue (non-volatile matter), mg/L	< 10	< 8
Density (20°C), g/cm <sup>3</sup>	0.7928	0.791 to 0.793
Permanganate number, min	> 30	> 60
Chloride as Cl <sup>-</sup> , mg/kg		< 0.5
Sulphur, mg/kg		< 0.5
Total iron, mg/kg		< 0.1

### Methanol Product

Al-Pac expects to sell approximately 2540 t/year of commercial grade methanol to external users. The remaining 1170 t/year of methanol will be used internally in the production of chlorine dioxide (ClO<sub>2</sub>), which is required in the pulp bleaching process.

The ClO<sub>2</sub> generator at Al-Pac currently uses IMPCA grade methanol; therefore, no issues are anticipated in the switch from purchased methanol to internally produced methanol. In the event that the methanol does not meet the IMPCA standard there is little concern as unpurified SOG was trialed in a pilot plant ClO<sub>2</sub> generator with no operational issues. Jemaa et al. showed that when using an unpurified SOG stream in a ClO<sub>2</sub> generator, ClO<sub>2</sub> production was not compromised [7].

### Return on Investment

The value of methanol in SOG as fuel is dependent on the amount of water vapour that it contains. Natural gas provides 50.5 MJ/kg (37.2 MJ/m<sup>3</sup>) heat of combustion, pure methanol provides 22.7 MJ/kg, and 50wt% methanol in SOG provides the equivalent of about 21.5 MJ/kg (the lower value for SOG is due to having to heat the water vapour it contains up to the combustion point operating temperature).

Therefore, if the purified methanol extracted from the SOG is burned, it will provide about 90,000 GJ/y; if fired in a lime kiln, it would directly displace this quantity of natural gas. With a 3-year average natural gas cost of C\$3.36/GJ, the heat contribution of the methanol is valued at just over C\$300,000 per year. At C\$410/t, the purchase/sale value of the purified methanol produced would be just over C\$1,500,000 per year; it can be seen that

the purified methanol is worth about five times as much as a commodity than as a combustion fuel.

The project was jointly funded by Alberta-Pacific Forest Industries and the Department of Natural Resources of Canada through the “Investments in Forest Industries Transformation” Program. The return on investment for Al-Pac is expected to be 24%.

## CONCLUSIONS

In addition to the economic benefits realized from purifying methanol from a waste stream source, there are significant environmental and process benefits. Methanol is generally produced from natural gas in facilities that are often a long distance from users. “Bio-methanol” produced at Al-Pac will replace the purchase of fossil fuel derived methanol and will eliminate the energy associated with transport. SOG incineration in the lime kiln will be also minimized, with the expectation that this will assist in alleviating kiln ringing and therefore production losses.

## REFERENCES

1. Der, B. and Jensen, A.S., A.H. Lundberg Systems Limited (Canada), “Methanol Purification Method and Apparatus”, International Patent WO 2010/091492 A1 (Pub. August 19, 2010).
2. Niemala, K., “Sulfur and Nitrogen Compounds in Rectified Methanol from Foul Condensate Stripping”, PAPTAC / Tappi International Chemical Recovery Conference Proceedings, Charleston, South Carolina, June 6-11, 2004.
3. Zhu, J.Y. et al., “Methanol Formation During Alkaline Wood Pulping”, TAPPI J., 83(7) (July 2000).
4. Bergstra, R., MTN Consulting Associates, “BioBased Methanol: A Market Study (Prepared for Alberta Pacific Forest Industries)”, August 22, 2008.
5. U.S. Federal Specification, O-M-232L, Methanol (Methyl Alcohol), Updated 4 January 2006.
6. International Methanol Producers and Consumers Association, IMPCA Methanol Reference Specifications, Updated December 9, 2010.
7. Jemaa, N., et al., FPIInnovations,(Canada),“Use of Chemical Pulp Mill Steam Stripper Off Gases Condensate as Reducing Agent in Chlorine Dioxide Production”, International Patent WO 2009/079746 A1 (Pub. July 2, 2009) and U.S. Patent 2010/0263816 A1 (Pub. Oct.21, 2010).



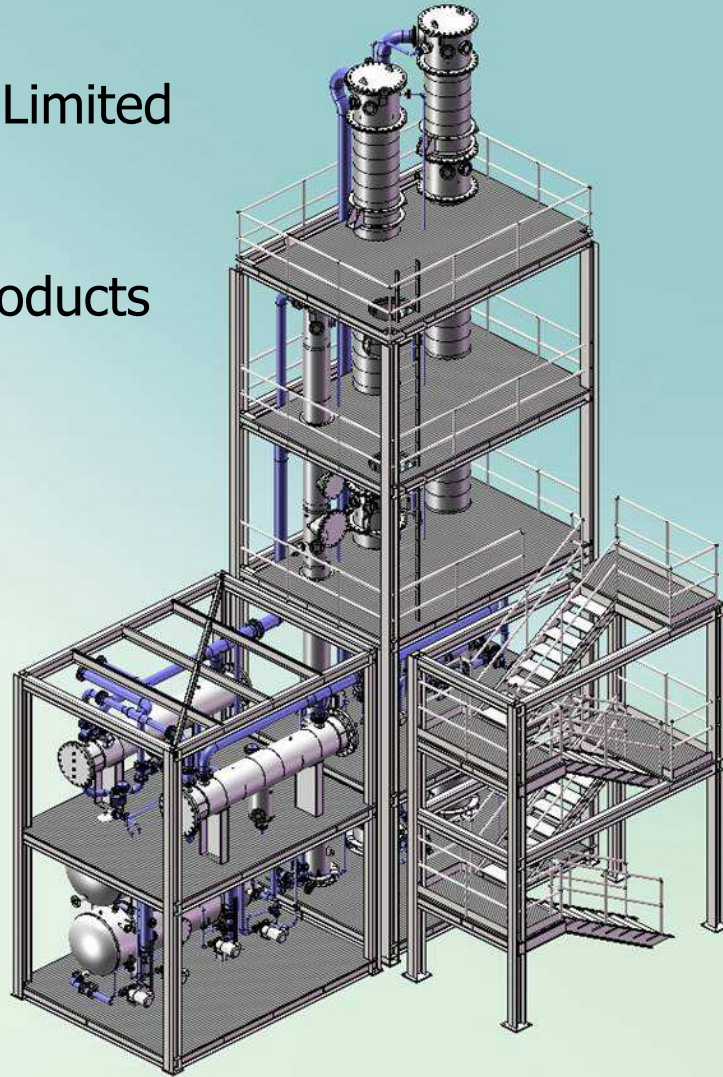
**Allan Jensen**

A.H. Lundberg Systems Limited

**Trevor Ip**

**Jamie Percy**

Alberta Pacific Forest Products



## Methanol Purification System

# Methanol in Kraft Pulping

- **By-product of the kraft pulping process**
  - Created in digester by chemical reaction
  - Hydroxyl ions reacts with lignin methoxyl groups
  - Leaves digester with extraction liquor or brown stock
  - Due to high relative volatility compared to water it is captured in digester and evaporator foul condensates

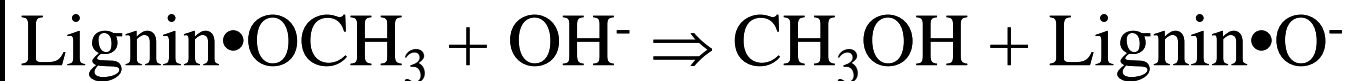
**Wood**



**Caustic Soda**



**Methanol**



# Methanol Formed

- **Wood Species**
  - Lignin methoxyl groups are more numerous in hardwoods than softwoods therefore more methanol is formed
- **Hydroxyl Concentration**
  - Higher alkali charge will produce more methanol
- **Temperature**
  - Higher cooking temperatures will produce more methanol
- **Time**
  - Longer cooking times will produce more methanol

# Stripping System

- **Steam stripping of foul condensate produces SOG**
  - Stripper Off Gas (SOG) typically consists of:
    - ~40% methanol
    - ~10% NCG, including TRS
    - ~50% water vapour
- **Must be designed to remove methanol**
  - Some stripping systems remove TRS only
- **Stripping system operation must be stable**
  - Consistent quantity and quality of SOG required
  - Stripping system should ideally be stand-alone, eg. not integrated with evaporator plant
  - Consistent cooling water temperature and pressure required; tempering pump on reflux condenser

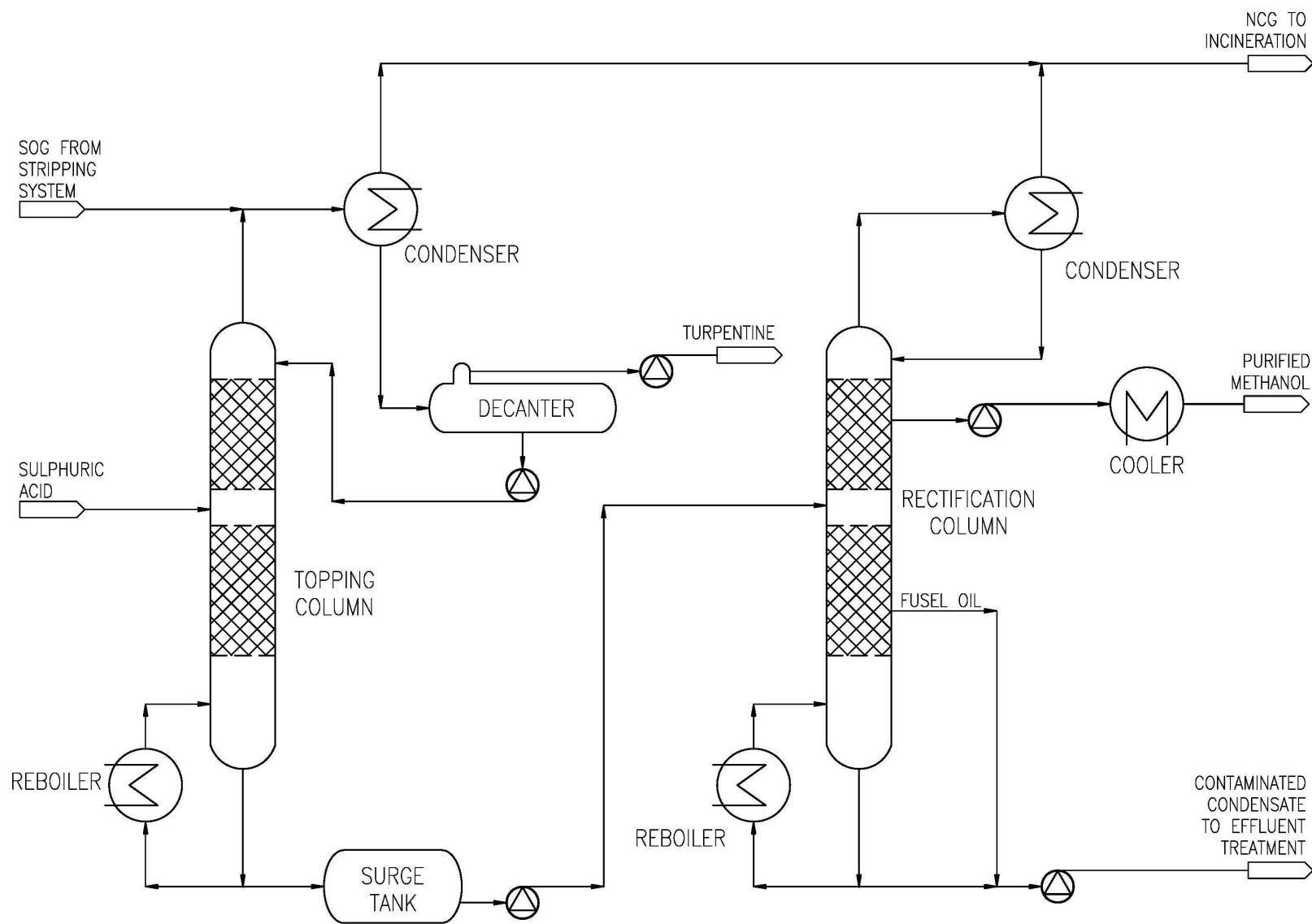
# Methanol from SOG

- **SOG composed of over 150 different substances**
  - Including various aliphatic alcohols and ketones, terpenes, and sulphur and nitrogen compounds
- **Methanol purification is based on distillation**
  - Numerous methanol systems in operation around the world; most are based on steam reforming of natural gas, followed by methanol synthesis and purification by distillation
- **Several design issues unique to methanol from SOG**
  - Azeotropes of methanol and organic contaminants
  - Immiscibility of terpenes
  - Dissociation of hydrogen sulphide and methyl mercaptan
  - Ammonia reacting to produce ammonium sulphate (fouling)

# Methanol Purification System

- **Two distillation stages**
  - Topping column to remove “low boilers”
  - Rectification column to remove water and other “high boilers”
- **Turpentine (red oils) recovery**
  - Decanter used to separate immiscible terpenes
- **Acidification**
  - Sulphuric acid added to maintain pH
- **Surge tank**
  - Operational flexibility, provides buffer between columns
- **Fusel oil recovery**
  - Remove intermediate boilers (ethanol, etc)

# Methanol Purification PFD



# Topping System

- **“Low boilers” stripped out in topping column**
  - Compounds with a lower boiling point than methanol at 65°C
  - Compounds with a high relative volatility
- **SOG condensed in topping reflux condenser**
  - NCG’s and “low boilers” vented back to SOG incineration system
- **Low pressure steam used in reboiler**
  - Heat recovered into demineralized water in reflux condenser
- **Surge tank**
  - 1½ hours retention allows operational separation of systems
  - Homogenizes feed flow to rectification system
  - “Topped” methanol can be recirculated to stripper feed tank



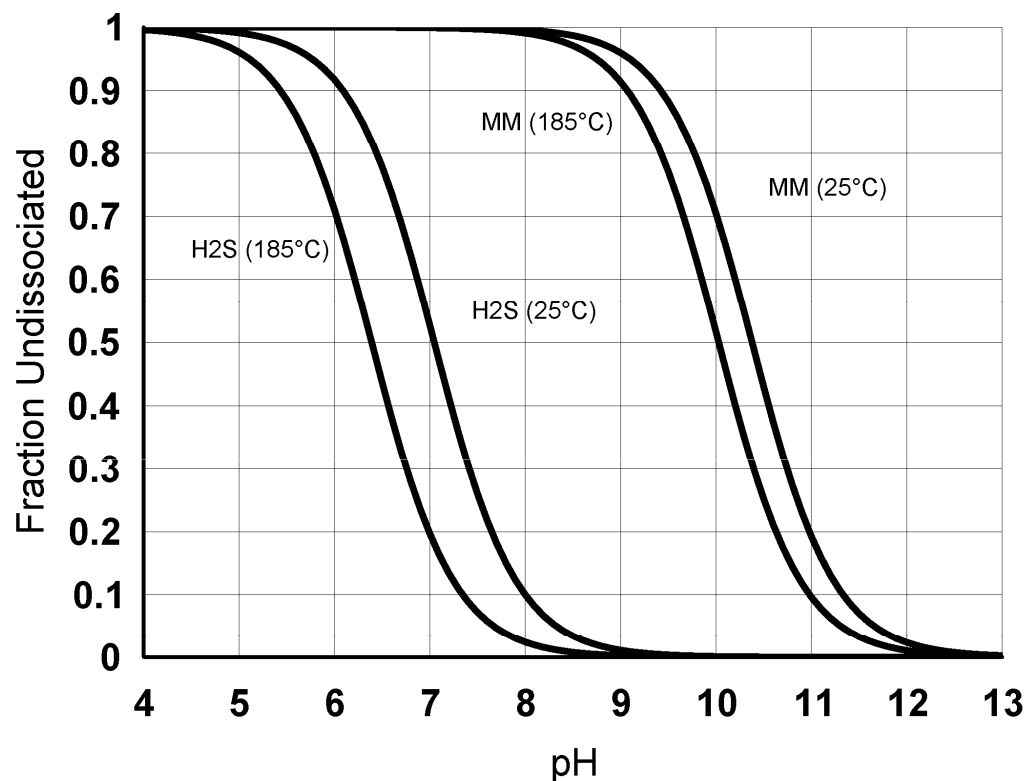
# Turpentine (Red Oils) Decanting

- **Turpentine recovery system required**
  - Some mills process turpentine through their stripping system and dispose of it with SOG incineration, this must be discontinued
- **Red oils recovered**
  - Using a decanter on the topping column reflux condensate
  - Directed to turpentine recovery
  - Red oils heavily contaminated with sulphur, if sold, they may need to be processed separately from regular turpentine
- **Methanol incineration**
  - If a turpentine incineration system exists, this can also be used to fire liquid methanol (eg. off spec, methanol tank full, etc)

# Acidification

- **Some contaminants dissociate at high pH**
  - In their dissociated form, compounds do not exert a vapour pressure and therefore cannot be removed by distillation
  - Condensed SOG typically has a pH of about 8 to 9
  - Hydrogen sulphide and methyl mercaptan dissociate into ions
- **Sulphuric acid is metered to the topping column**
  - Target pH of about 5 to 6
  - Ammonia in SOG will react with acid to produce insoluble ammonium sulphate (fouling)
  - The highly volatile ammonia easily strips out in top of column
  - Acid added at the mid-point of the column

# Dissociated Compounds



**Methyl  
Mercaptan**

**Hydrogen  
Sulphide**



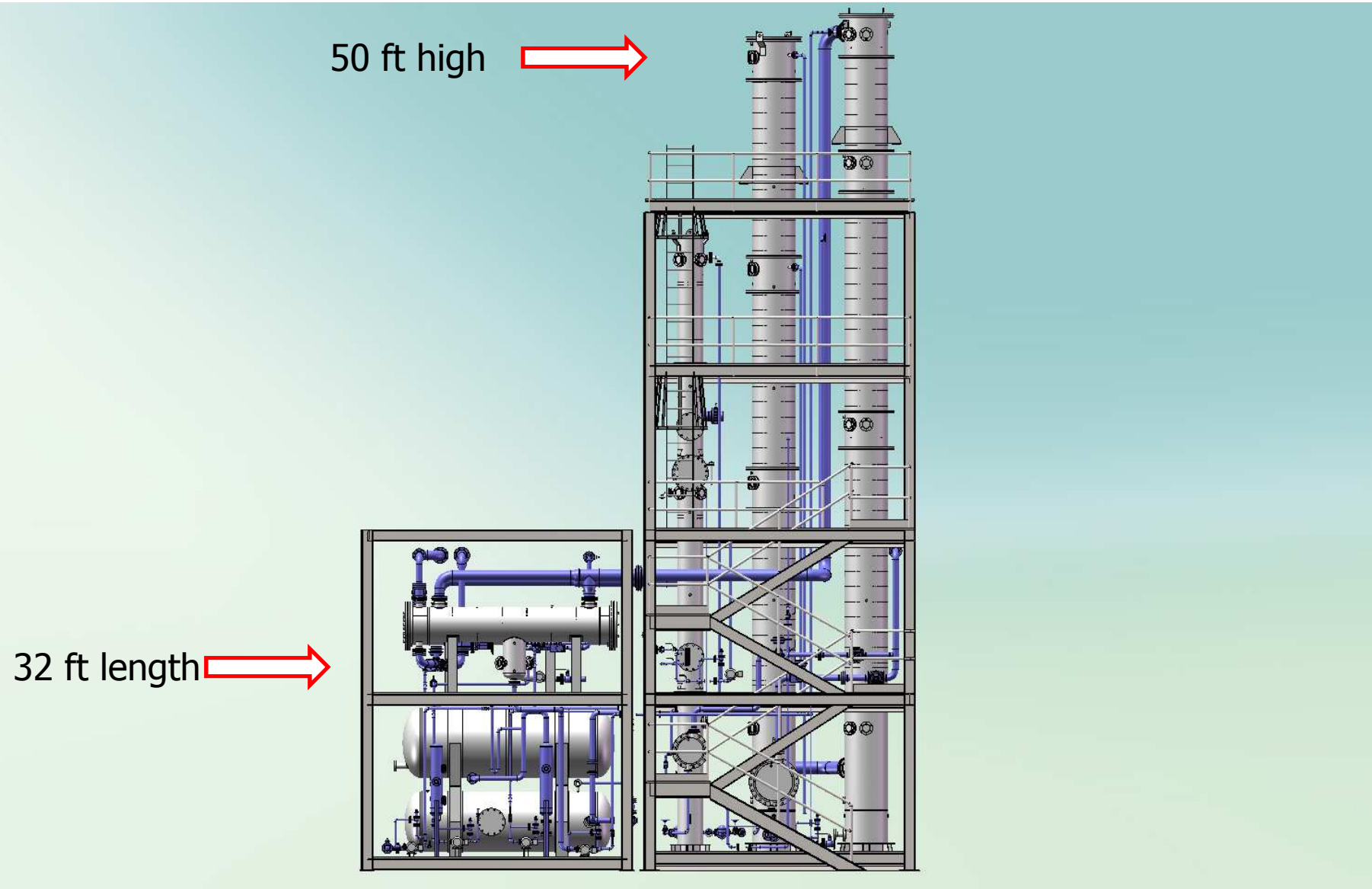
# Rectification System

- **“High boilers” removed in rectification column**
  - Compounds with a higher boiling point than methanol (water, ethanol, etc) removed in bottoms
- **“Intermediate boilers” removed as fusel oils**
  - Higher alcohols (primarily ethanol), higher ketones, etc.
  - Drawn off from the column slightly below the feed point
  - Sacrifice 2 to 3% of methanol product
- **Methanol product withdrawn slightly below top**
  - “Low boilers” not removed in topping system removed from top of rectification column
  - Methanol product can be pumped to storage, recirculated to stripper feed tank or surge tank, or incinerated in lime kiln

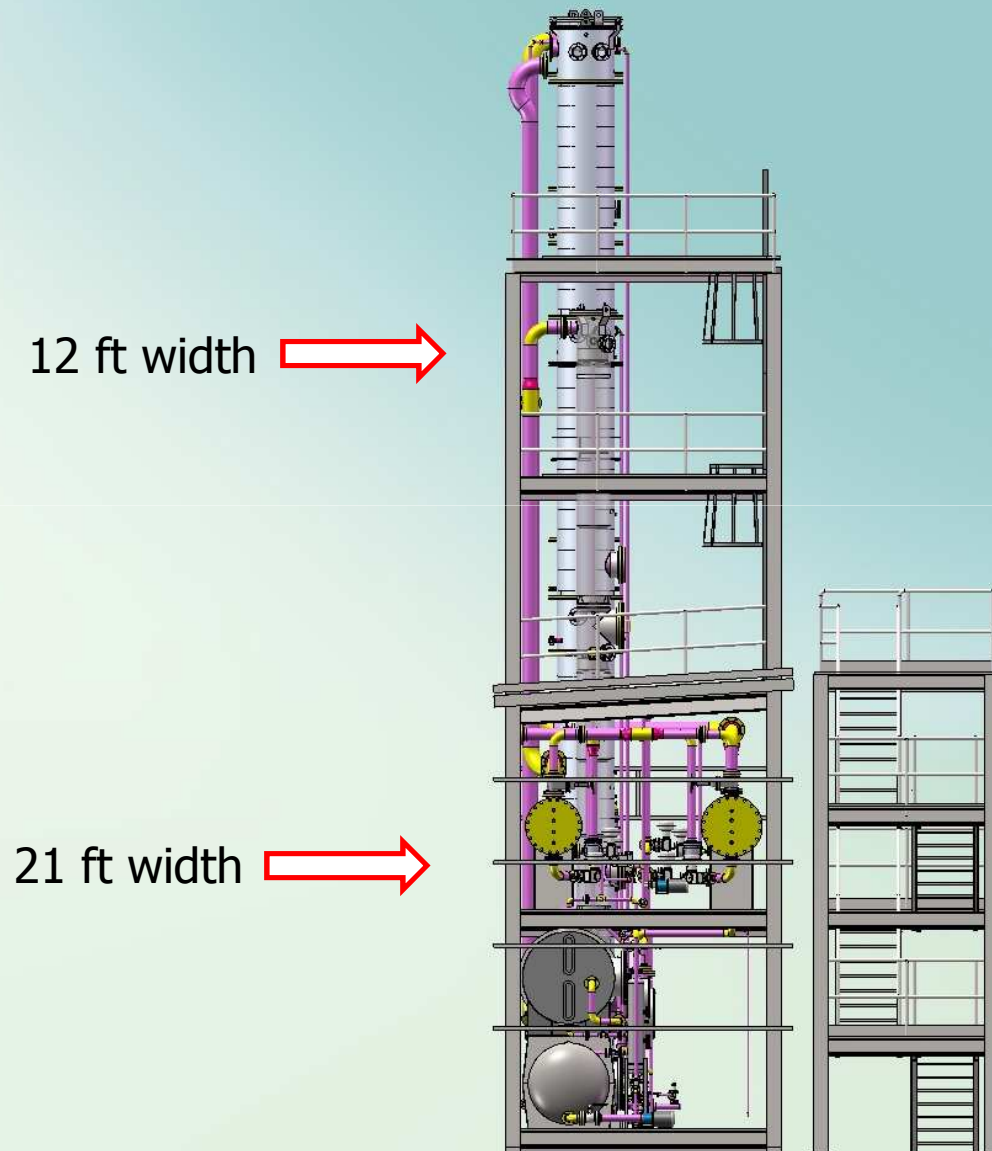
# Equipment

- **Designed to process up to 700 kg/h methanol**
  - Minimal cost savings for a smaller system
- **System supplied in three modules**
  - Distillation columns
  - Condensers and tanks
  - Stairway
- **Modules include**
  - Steel skid
  - Equipment
  - Piping and handvalves
  - field instrumentation
  - Insulation

# Module: Front View

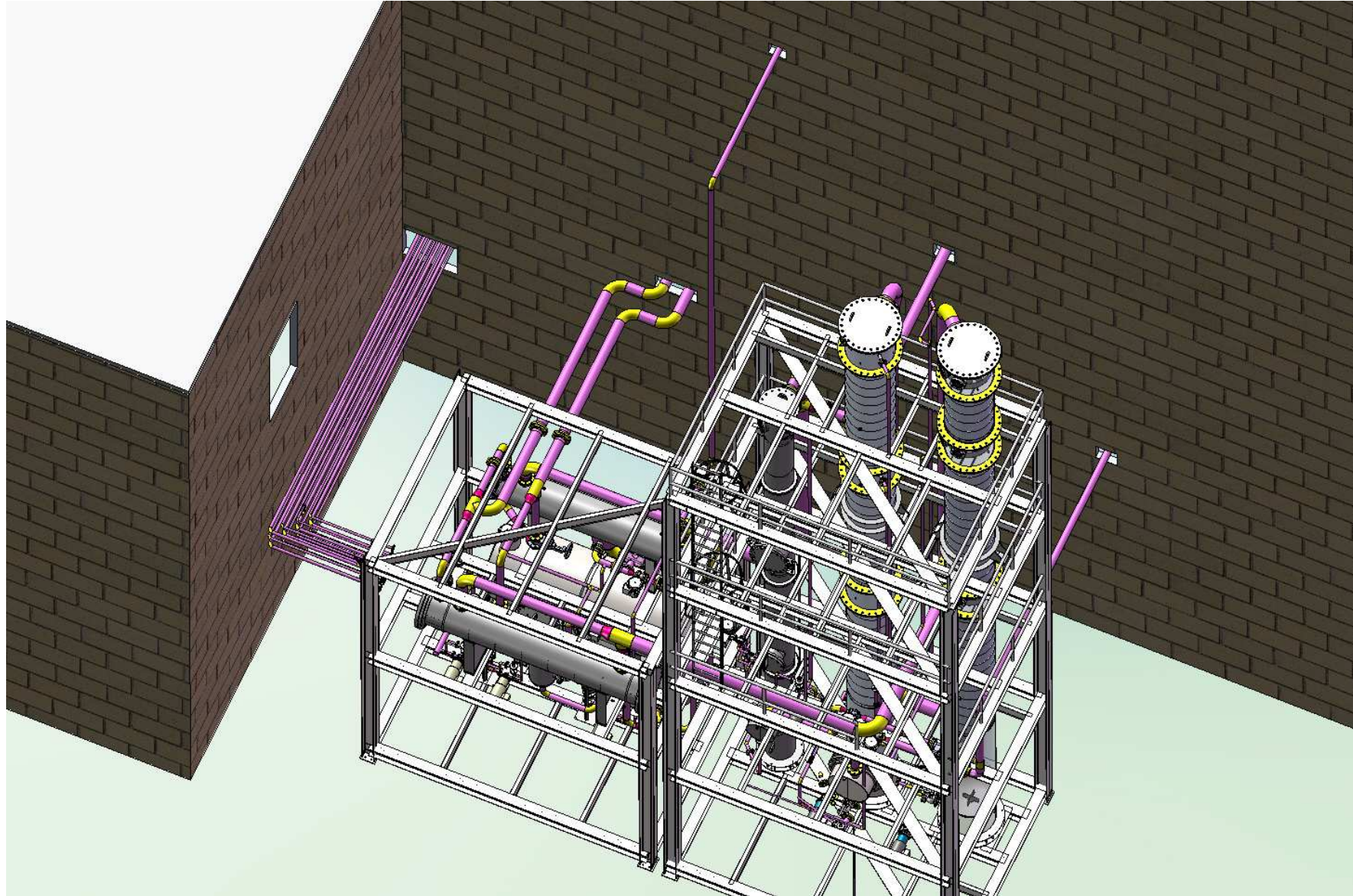


# Module: Side View



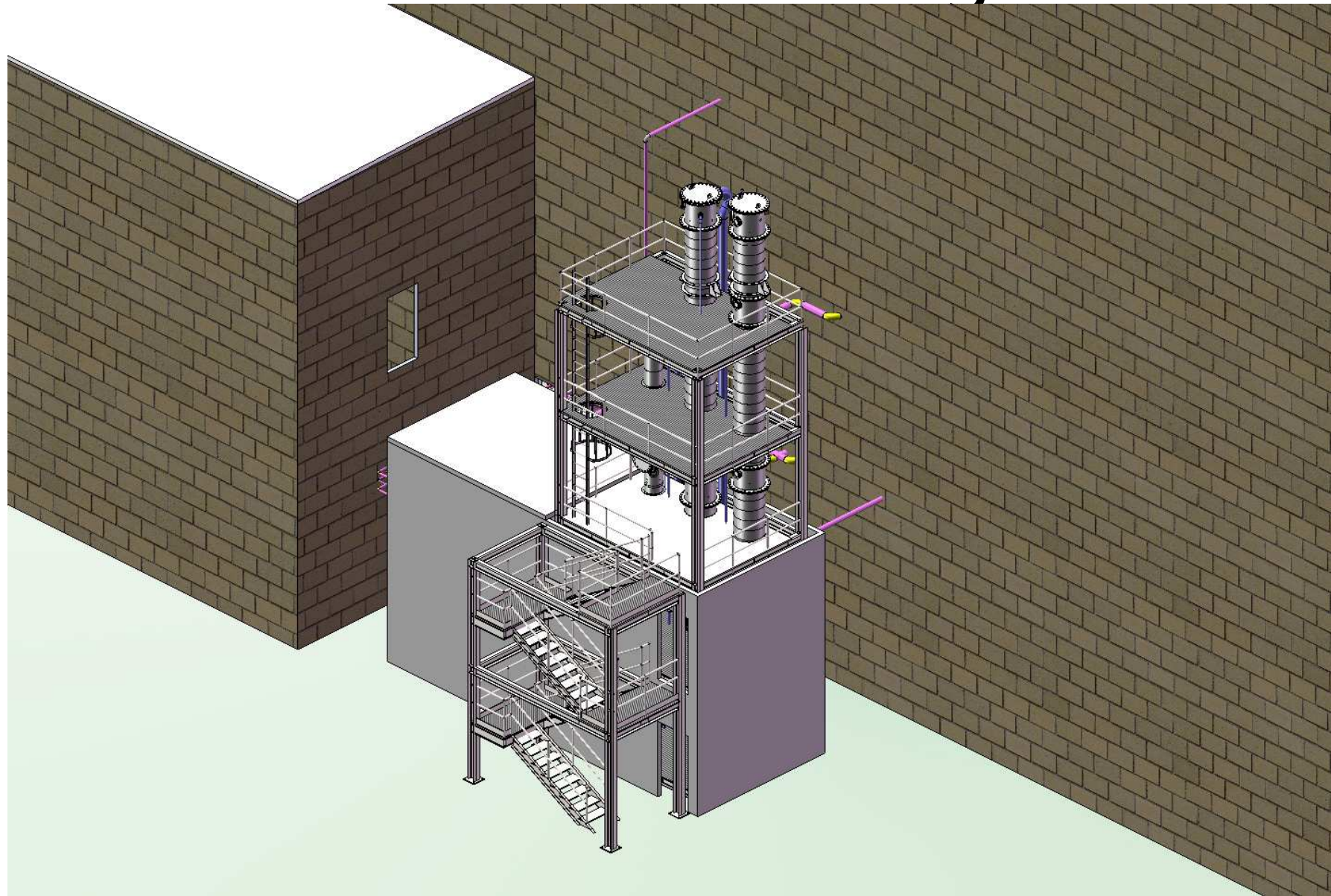


# Module: Installation





# Module: Cladding

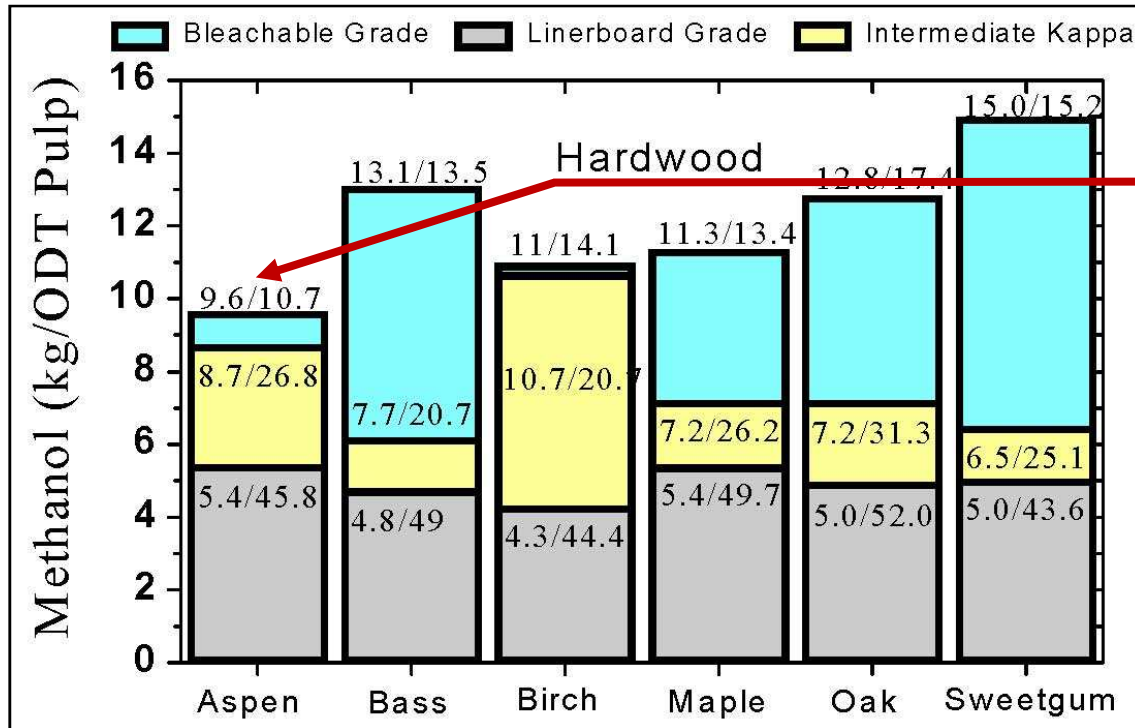




# Module: Installation



# Methanol From Hardwood



~9 kg methanol/ADt pulp is formed by pulping Aspen

(Zhu et.al, Methanol formation during alkaline wood pulping," Tappi Journal, July 2000)

- Production of 600,000 ADt/y at Al-Pac = 5400 t/y methanol formed
- Large fraction of methanol captured in foul condensate
- Steam stripping concentrates methanol into SOG
- About 3700 t/y expected to be recovered as purified methanol

# The Value Of Methanol

- **SOG as a fuel**

- Methanol provides 22.5 MJ/kg heat of combustion
- Natural gas provides 50.5 MJ/kg
- If 3700 t/y methanol burned= ~90,000 GJ/y
- At natural gas cost of C\$3.36/GJ (3 yr avg.), methanol has thermal value equivalent to ~C\$300,000/y

- **Methanol as a chemical commodity**

- Commercial grade methanol C\$410/t (3 yr avg.)
- If 3700 t/y methanol sold = ~ C\$1,500,000/y
- Approximately 5x the value over burning

# Commercial Grade Methanol

Typical standards include International Methanol Producers & Consumers Association (IMPCA) and Federal Grade AA

IMPCA Test	Target
Purity	> 99.85 wt %
Water	< 0.1 wt %
Ethanol	< 50 mg/kg
Acetone	< 30 mg/kg
Chloride	< 0.5 mg/kg as Cl <sup>-</sup>
Sulphur	< 0.5 mg/kg
Acidity	< 30 mg/kg as acetic acid

# Methanol Utilization

- **Chlorine dioxide production**
  - Methanol used as reducing agent in  $\text{ClO}_2$  generator
  - ~1170 t/y methanol required at Al-Pac
- **Other uses**
  - ~2540 t/y available for:
    - External sale
      - Solvent
      - Formaldehyde, MTBE and acetic acid production
      - Transportation of natural gas by pipeline
    - Auxiliary fuel
    - Biodiesel production from soap

# Conclusions

- **Cost benefits**
  - Return on investment expected to be 24%
- **Process benefits**
  - Alleviate kiln ringing from SOG firing
- **Environmental benefits; GHG reduction**
  - “Bio-methanol” replaces fossil fuel derived methanol
  - Locally produced; reduction in transport requirements



# Questions?

