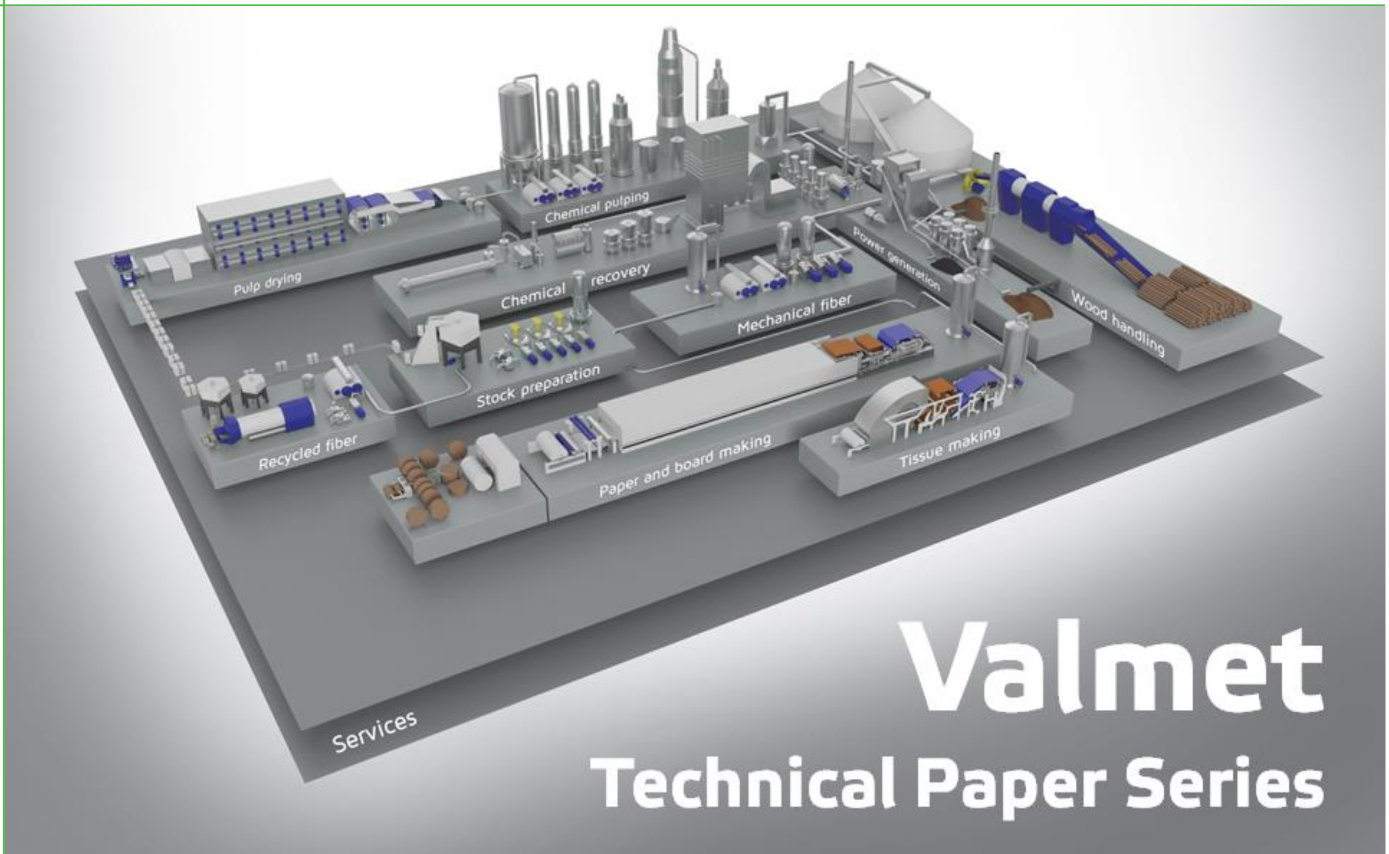

Methanol, from waste byproduct to valuable fuel

Executive Summary

Methanol in mill condensates is considered by most pulp mills in North-America to be a waste byproduct of the pulping process that needs to be disposed, either through the effluent treatment system or by incinerating the stripper off gases (SOG), often using the lime kiln as the incineration point. Incineration of SOG in the lime kiln can cause problems in kiln operation due to the high moisture content of SOG and the variability in the amount of SOG produced, which has been linked to ring formation and capacity issues for the kiln. Most mills in Europe have instead adopted an approach where they liquify the methanol, removing a significant amount of water and making it an easier fuel to handle that can be properly combusted in a controlled manner.

Recently, methanol is also being looked at as a possible green transportation fuel. While burning in the kiln does not require additional purification steps, the nitrogen and sulfur content of the methanol needs to be reduced to allow its usage as a transportation fuel.

This paper reviews the technology that has already been used for several years to liquify methanol from the SOG and the new process that has been developed to produce purified methanol that can be sold as a green renewable fuel, transforming an undesirable waste byproduct into a potential new revenue stream for the pulp mill.

Introduction

Methanol is produced during the cooking process in Kraft pulp mills. It is released from the wood in the digester and is transferred to the weak black liquor and to the flash vapor from the blow tank. This flash vapor is then condensed in blow heat recovery in the form of foul condensate (digester condensate). During evaporation, the methanol present in the weak black liquor is flashed and condensed into the evaporator condensate. Methods for the removal or disposal of the methanol present in the mill condensates vary. In North-America, these removal or disposal methods consist of sending the contaminated condensate to the secondary effluent treatment system where it will be handled as BOD, or to treat the contaminated condensate in a stripper system that will release the methanol as SOG. Most mills using a stripper will then incinerate the high moisture content SOG (typically 35% methanol and 65% water). A few mills will condense the SOG to produce a lower moisture (around 15-20% water) liquid methanol stream that can be stored and burned as needed in a more controlled fashion. This simple condensation of the SOG leaves it fairly contaminated with nitrogen (as ammonia) and TRS compounds, limiting its potential usage. This paper will focus on the benefits of converting the methanol to a liquid and on new technology that is available to purify the methanol that makes it suitable as a green fuel or chemical for external sale, adding value to what is normally considered a waste product.

A typical Kraft mill produces between 10 to 15 kg of MeOH (methanol) per ton of air dry pulp (ADT) from the digester. Assuming a pulp yield loss of 10% between the outlet of the digester and the finished product, this corresponds to between 11 and 16 ton/day of methanol for a 1000 ADMTP mill. If the mill does not operate a condensate treatment system, the methanol in the digester condensate and the evaporator foul condensate is discharged to the effluent treatment system to be treated as BOD. The impact from sewering these condensates and the associated methanol are increased cost of treatment (biosludge production, power requirements for pumping and treatment, additional water consumption) and the loss of heating value of the methanol as a fuel.

Pulp mills condensates

Most pulp mills have two main condensate production areas; the blow-heat recovery system at the digester(s) and the evaporators. Some newer mills have blow-heat recovery integrated into the evaporators and will only have evaporator condensates to handle. Most evaporator train designs allow for the segregation of the condensates into three fractions (clean, intermediate and foul) and concentration of the methanol into the smaller fraction of foul condensate. Foul condensate is typically 10% of the evaporator condensate for a modern evaporator train. Using a condensate treatment system, it is possible to reduce the methanol content of the foul portion of the condensate to the point where this treated condensate can also be reused in the mill. Modern evaporation plants are designed not only for concentrating black liquor for combustion in recovery boilers, but also for producing various clean condensate streams that can be reused 100 % in the pulp mill to minimize overall water consumption (Wernqvist 1995, Wernqvist et al 2017). Clean, intermediate clean, and treated condensate streams from the evaporation plant are typically reused as wash and/or dilution water in the fiberline and in the causticizing plant.

In modern evaporation plant upgrades, condensate handling is customized for the specific mill, combining several measures (Stern et al 2006), such as:

- A larger condensate treatment plant, such as a high-volume stripper, integrated into the evaporation plant in an energy-efficient configuration (figure 1).
- Proper arrangement of the incoming vapor to the evaporator and separate condensation zones, to ensure good condensate segregation in the back-end effects. It is critical that vapor be fed to the lower part of the heating shell (figure 2). How much "foul" condensate is formed, depends on the

relative heating surface areas in the "clean" and "foul" zones. Quantities of methanol and other volatiles in the vapor that end up in the "foul" condensate fraction are determined by the equilibrium conditions (Redeborn et al 1998).

- One or more Tube Evaporators in the plant may also be equipped or retrofitted with an internal condensate treatment (ICT) system (figure 3), in which condensate may be recycled and treated in a "clean stripping" zone inside the evaporator effects (Stern et al 2006).

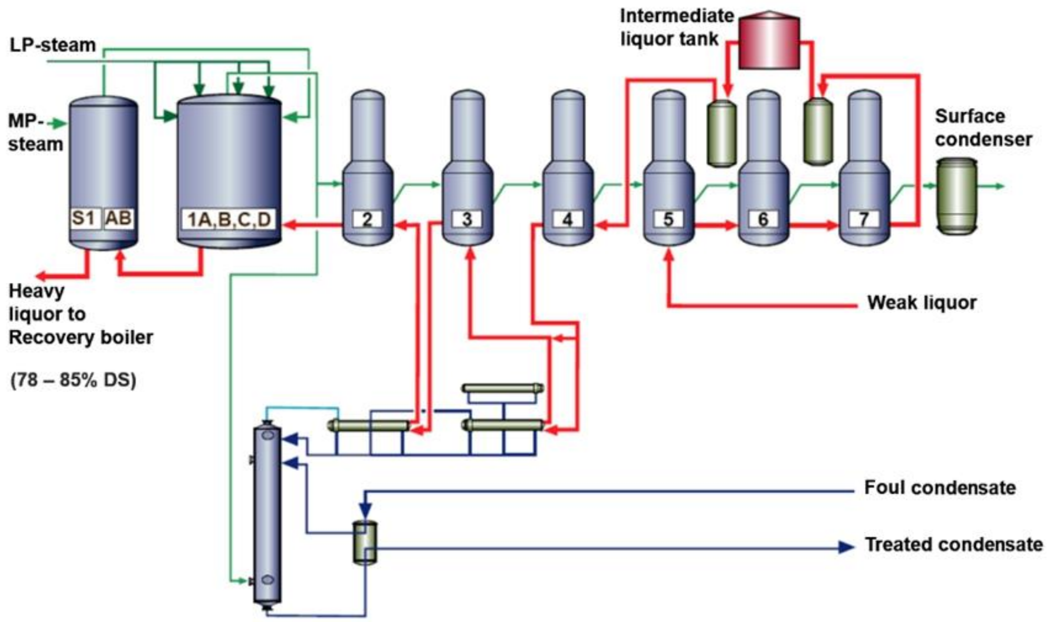

Figure 1. CFB process overview

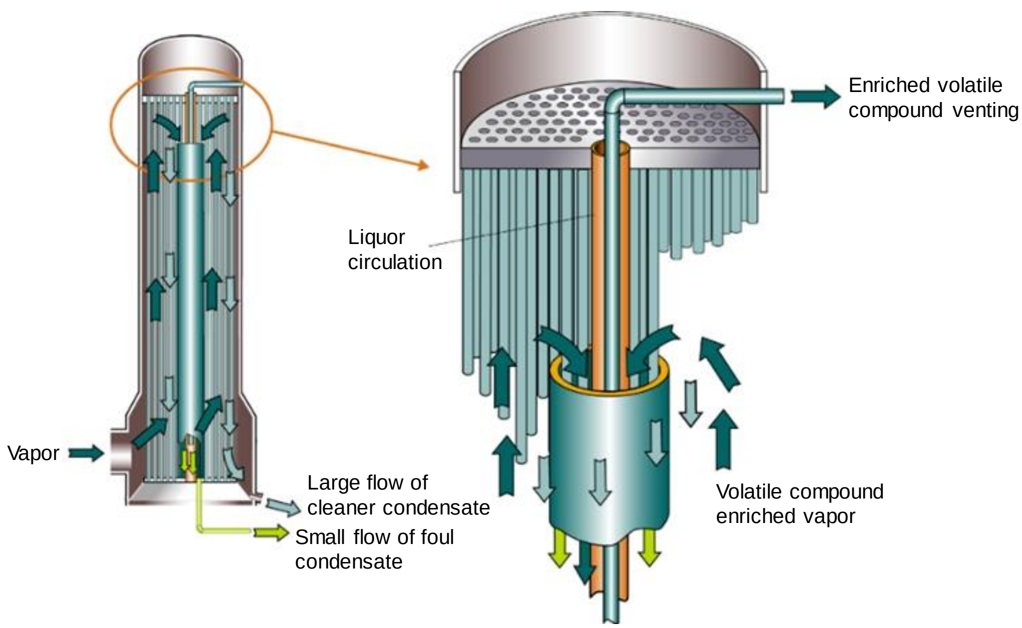

Figure 2. Internal condensate segregation in modern tube type evaporator vessel to produce clean condensates for recycling in the mill (Tikka 2008)

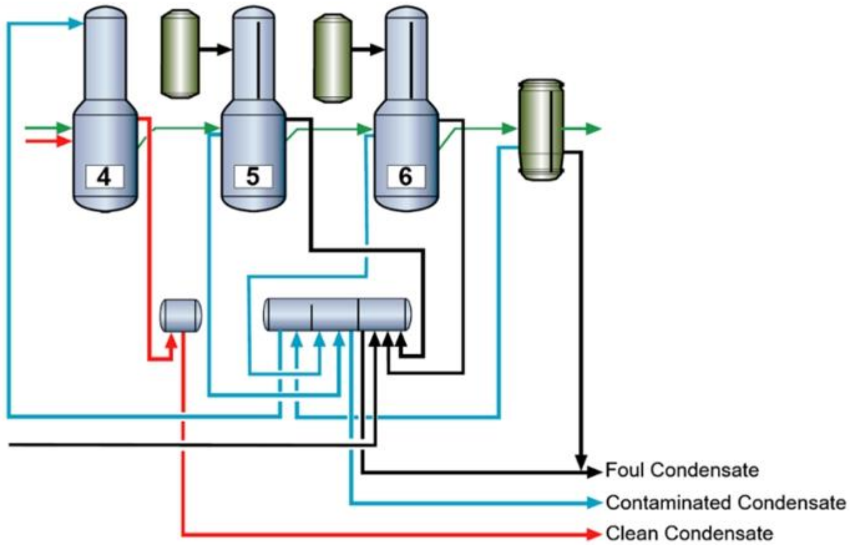

Figure 3. Condensate Segregation with ICT to maximize the clean condensate fraction

Condensate treatment for methanol recovery

Most modern mills will use a condensate treatment system to remove the methanol from the digester and evaporator foul condensates. **Figure 4** shows how condensates are handled in a modern mill.

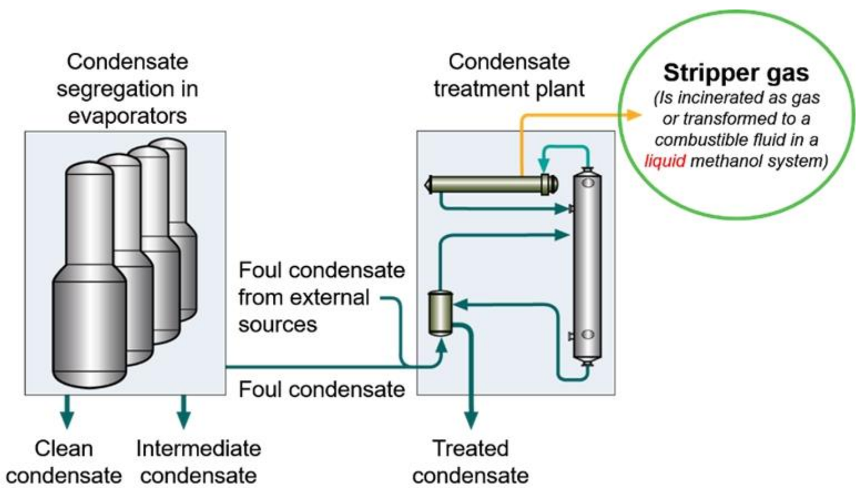

Figure 4. Condensate handling and SOG production

The treatment system involves a stripping column where the condensates flow counter current to either live steam or vapor from the concentrator. This releases the methanol into a gas form called stripper off gas (SOG). After some steps of heat recovery, that also reduce the moisture content of the gas to around 65% (or 35% methanol concentration), the SOG is sent to either incineration, typically to the lime kiln or to the recovery boiler, or to a liquid methanol system.

Problems associated with SOG incineration

Direct incineration of the SOG is not thermally efficient, however, due to its high moisture content and needs to take place as the SOG is produced as the gases cannot be stored. Burning SOG in the lime kiln can have other negative impacts as the SOG will not be a constant flow, which will cause variation in the kiln temperature profile. These changes in kiln temperature profiles have often been associated with the formation of rings and reduced capacity and availability of the lime kiln (Tran 2016). Similarly, introducing more moisture in the recovery boiler increases the amount of flue gas to be handled, and flue gas volume is often a factor in the recovery boiler capacity and fouling tendencies.

Producing liquid methanol

Most mills outside of North-America as well as many mills in North-America use an enrichment and condensation system to produce liquid methanol (**Figure 5**).

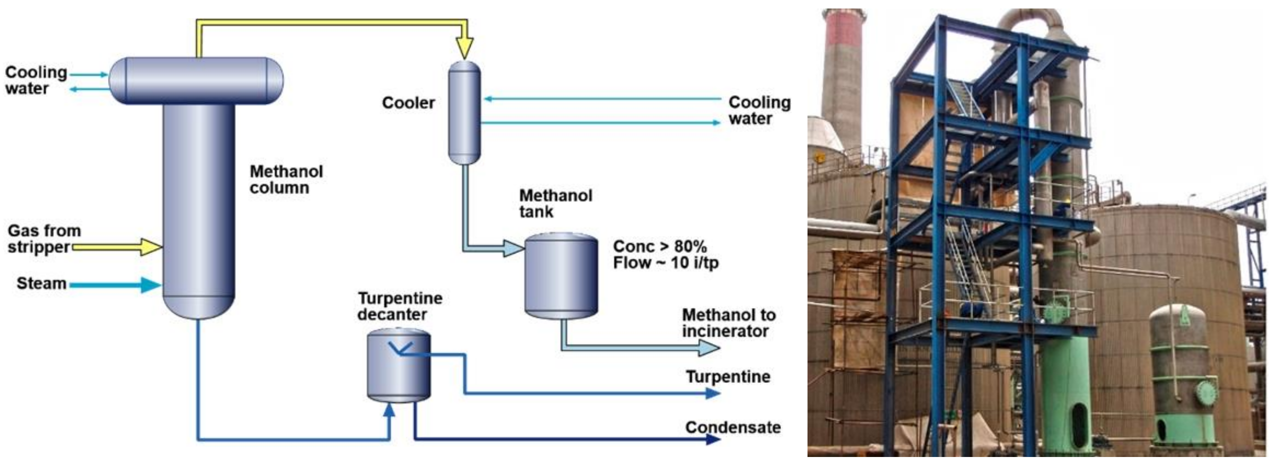

Figure 5. Typical liquid methanol system

This condensation process reduces the water content of the methanol to around 20% and liquified methanol can be easily stored for use as needed. Liquid methanol is also considered to be a green fuel and can be used to displace natural gas or oil either as part of the main fuel or as a start-up fuel. Several of the recent new pulp mills that can operate without any fossil fuel, use stored liquid methanol for start-up of combustion equipment. As shown in the mini-flowsheet above, a typical liquid methanol system consists of a partial condenser operated with low pressure steam. Cooling water is used in the upper part of the vessel to maintain a temperature that will be below the condensation point of water while remaining above the boiling point of methanol. The steam is injected at the bottom of the column to remove more methanol from the condensate that forms in the upper part of the vessel. The rich methanol vapor is then directed to a water-cooled condenser that produces liquid that is around 80% methanol in concentration. The water condensate from the system is sent back to the condensate treatment system.

Issues with untreated methanol

One problem with liquid methanol produced from condensing untreated SOG is the high nitrogen content, mostly as ammonium, and the sulfur content in the form of TRS. Incineration of SOG or untreated liquid methanol leads to higher NOX and SO2 emissions. Untreated liquid methanol has a very strong unpleasant odor, making handling more difficult. Commercially available methanol is primarily made from natural gas and is not considered a green (carbon neutral) fuel. In Europe, there is currently a demand for green or forest based methanol, as both a transportation fuel and a chemical. For example, Stena Line is converting some of its ships to run on locally produced methanol.

Purifying pulp mill methanol

Valmet, in partnership with other industry partners, has developed and demonstrated a process to treat SOG before producing liquid methanol. This purification process, called PuriMeth, removes nitrogen and sulfur from the SOG upstream of the first condensing and water removal stage in the liquid methanol plant. A demonstration plant of the SOG purification system was installed at the Metsä Board, Husum mill (Wennberg et al 2017). The system was equipped with a complete control system for continuous and long-term operation in an industrial environment. Different process configurations were evaluated to optimize the quality of the methanol and to demonstrate long term stable operation.

The purification process uses sulfuric acid to convert the gaseous ammonium to ammonium salts. The addition of acid also promotes the separation of TRS components. The system needs to be operated in the proper condition to avoid polymerization of the residual turpentine. The plant was operated for almost 1000 hours of trouble-free operation and over 99% ammonium removal was achieved. The sulfur and nitrogen content of the liquid methanol were below 50 mg/l in both cases. Following this demonstration project, the design of a full-scale methanol purification system was completed and is now commercially available for pulp mill applications.

Economic considerations

The economics of methanol liquification and purification will vary based on each specific mill situation. For example:

- Pure methanol has a HHV of 22.7 MJ/kg (9760 Btu/lb). 90% recovery for a 1000 ADMTPD mill would lead to 10 to 15 ton/d of methanol with an energy value of between 80,000 to 120,000 GJ per year.
- If the methanol was previously incinerated as a gas with high moisture content, it likely provided only marginal heat input. By comparison, burning liquid methanol allows to possibly displace fuel oil or natural gas. Using 100,000 GJ of methanol, a carbon neutral green fuel, as opposed to natural gas, would provide a reduction of roughly 5,000 tons of CO2, in addition to the savings in not having to purchase the equivalent natural gas. Avoided CO2 emissions would be higher if displacing fuel oil.
- For a mill that has access to a market for purified methanol, fossil methanol currently sells for around US$500/ton ("Historical Methanex Posted Price", September 2018). At 10 ton/day of production, this is roughly US$ 1.8 million annually. Bio-methanol would likely command a premium compared to fossil based methanol.
- For a mill that has no good location for burning methanol as a gas (overloaded recovery boiler or operating problems if incinerated in kiln), producing liquid methanol could eliminate operating issues related to its disposal.
- Removing methanol from the mill condensates reduces effluent treatment costs and can also lead to reduce fresh water usage if the quality of the cleaner condensates produced allow their reuse in the process.

Conclusions

Methanol produced in a Kraft pulp mill can be more than a waste that requires disposal. If properly segregated, removed from the mill condensates and made into a liquid fuel, it becomes a green fuel that can be efficiently combusted in the lime kiln or in other boilers. It can also be stored and become a start-up fuel for mills that want to further reduce or eliminate their fossil fuel usage. Adding an extra step to purify the methanol prior to making it into a liquid also offers the potential to sell green methanol that can be used as a transportation fuel or as a feedstock in the chemical industry.

The potential economic incentives for a pulp mill to remove methanol from the mill effluent and to convert it to liquid form are lower effluent treatment costs, lower water consumption with additional condensate recovery and reuse, lower energy cost through lower water consumption and better energy value in the methanol as a liquid, and the potential of an additional revenue stream with purified methanol as a product for outside sale. Conversion of methanol into a liquid is well proven commercially available technology. Methanol purification is now well proven as well and ready for commercial applications.

REFERENCES

Redeborn M., Wernqvist A., Ström K. (1998): Nord. Pulp Paper Res. J. 13:3, 172– 179, “Adaptable calculation method for segregation of contaminants in vapours formed from black liquor”.

Stern R., Anängen F., Wernqvist A. (2006): Proceedings 2006 Tappi Engineering, Pulping, & Environmental conference, Atlanta, Nov. 6–8, 2006, “Evaporation system solutions – Energy and the environment”.

Tikka P. (2008): Papermaking Science and Technology Book 6 (Part 2) Chemical Pulping Part 2, Recovery of Chemicals and Energy. Second edition. Paper Engineers' Association/Paperi ja Puu Oy. ISBN 978-952-5216-26-4.

Tran H. (2016): TAPPI Kraft Recovery Course, “Lime kiln chemistry and effects on kiln operations”.

Wennberg O, Guordon M, Svensson M, Sjödin H, Nordlander T, Brücher J, Blomberg Saitton D (2017): International Chemical Recovery Conference 2017, Halifax, Canada, “Purification of SOG – An industrial demonstration”.

Wernqvist A. (1995): Proceedings “28th Pulp and Paper Annual Meeting. ABTCP, Sao Paulo, SP — Brazil. Nov. 1995“, pp. 607–621, “On condensates in tomorrow’s environmental-friendly Kraft pulping mill”.

Wernqvist A., Burelle R., Stern R., Vedin F., Krus C-J., Fransson A. (2017): Proceedings TAPPI Peers, Norfolk, Virginia, Nov. 5-8, 2017. ”Expansion of chemical recovery capacity at Södra Cell Värö mill”.

“Historical Methanex Posted Price”, Pricing for Liquid Methanol, North American Region, available as a pdf file at www.methanex.com/our-business/pricing (2018 pricing ranges from 479 USD to 506 USD/MT, September 2018 pricing is 485 USD/MT).

This white paper combines technical information obtained from Valmet personnel and published Valmet articles and papers.

Valmet provides competitive technologies and services to the pulp, energy and paper industries. Valmet's pulp, paper and power professionals specialize in processes, machinery, equipment, services, paper machine clothing and filter fabrics. Our offering and experience cover the entire process life cycle including new production lines, rebuilds and services.

We are committed to moving our customers' performance forward.