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# TRANSFORMING PULP MILLS INTO BIOREFINERIES THROUGH RENEWABLE METHANOL PRODUCTION

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## ABSTRACT

The scarcity of renewable chemicals in the market demands new solutions and ambitious development targets from all industries. To answer the global need for biochemicals, pulp mills can play an important role. Pulp mills are already converting biomass to a variety of sustainable products, but in the future, they could be major producers of biochemicals.

In a pulp mill, along with pulp, biomethanol is produced as a by-product through demethoxylation of lignin. By refining and purifying the raw methanol further, commercial grade methanol is produced and this high-quality biochemical is an important raw material for various industries. This is by far the most cost-efficient way to add renewable chemicals into the fossil-source dominated market. Producing biomethanol by valorizing pulp mill side streams is the first step and paves the path to possible e-methanol production in the future. Pulp mills could truly be biorefineries by utilizing their surplus electricity and biogenic $CO_2$-emissions to produce sustainable and valuable product, e-methanol, in the future. With this paper, we would like to convey the story of renewable methanol production at pulp mills.

**Keywords:** biomethanol, biorefinery, circular economy, carbon capture, electrolysis, e-methanol

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## INTRODUCTION

Recently, pulp mills have widened their product portfolio by expanding their operations beyond pulp production. Incorporating the production of value-added products to pulp production, enables pulp mills to transform into biorefineries. One of the potential product sectors is advanced biofuels or RFNBOs, and pulp mills can act as a versatile platform for a variety of chemicals, especially methanol. Methanol is a widely utilized commodity chemical and a common building block for synthesis of other chemicals. Alternative potential purpose for methanol is utilization as a transportation fuel as a drop-in fuel or mixed with other chemicals, such as gasoline, or utilize it as a raw material for biodiesel production. Figure 1 illustrates the global methanol production and utilization as a precursor for a variety of chemicals.

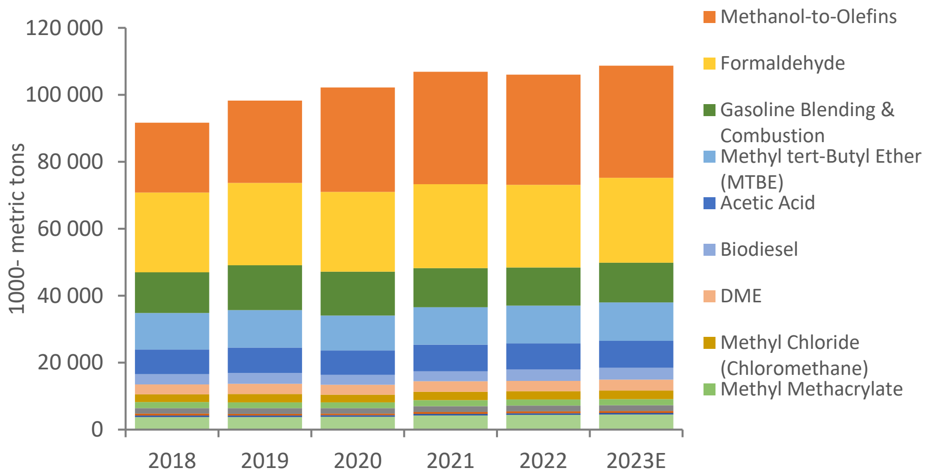


*Figure 1. Global methanol production and utilization [1].*

Pulp mills are already producing methanol during their normal operations: methanol is formed as a by-product at pulp mills during normal pulping processes. Methanol is primarily formed during the sulphate cooking phase, where methanol is eliminated through alkali-catalysed reactions involving the 4-O-methylglucuronic acid residues present in hemicellulose. Additionally, methanol can also be produced through oxidation reactions occurring in phenolic lignin during the $O_2$-delignification process.

The amount of obtained methanol varies depending on different factors, such as the wood type and the pulping process, the yield typically ranging from 6-15 kg/ADt. During the cooking process, the reaction between the sulphide and hydrogen sulphide ions and lignin leads to the formation of organic sulfur compounds. These compounds, including methanol, end up in the black liquor, a by-product of the pulping process. Due to its high volatility, methanol, along with water and other volatile compounds, volatilizes and becomes part of the foul condensate during the evaporation stage of the black liquor.

To convert the impure and odorous raw methanol into valuable compound, ANDRITZ has developed a methanol purification process which produces methanol with 99,99 mass-% purity utilizing the raw methanol collected from the evaporation plant. The methanol purification process removes impurities, such as sulfur and nitrogen, from the raw methanol. Additionally, ethanol and acetone are removed to achieve the high biomethanol quality requirements for external utilization. The methanol purification plant is a cost-effective way of upgrading the raw methanol into high quality biomethanol directly at the pulp mill.

Combining carbon capture technologies with $H_2$ generated with renewable energy and synthesis to for example, e-methanol, is an opportunity for a pulp mill to produce also RFNBOs and possibly take advantage of integration benefits with raw methanol purification. The largest sources of $CO_2$ emissions derive from recovery boiler, the power boiler, and the lime kiln, where $CO_2$ is generated through combustion processes. Majority of the $CO_2$ produced at pulp mills is biogenic due to biomass utilization in combustion. With carbon capture, pulp mills could turn their $CO_2$ emissions into valuable renewable methanol by applying methanol synthesis process. Methanol synthesis combines the utilization of captured carbon from the mills and hydrogen produced via electrolysis. The future abundance of renewable and low-emission electricity increases the attractiveness of electrolysis process, where the feasibility is highly dependent on electricity price.

Renewable fuel production and consumption are dependent on the regulatory framework and different policies, which affect the prices of biofuels, emission calculations and consumption targets in the future. These policies can improve the attractiveness of renewable methanol production from pulp mills.

## PULP MILL AS A MAJOR RENEWABLE METHANOL PRODUCER

Pulp mills are versatile platforms for producing a variety of bioproducts, advanced biofuels and RNFBOs by combining the available resources and new innovative technologies. Figure 2 presents a concept for the biorefinery of the future, where pulp mill is a major pulp producer and simultaneously a major methanol producer by combining various available technologies.

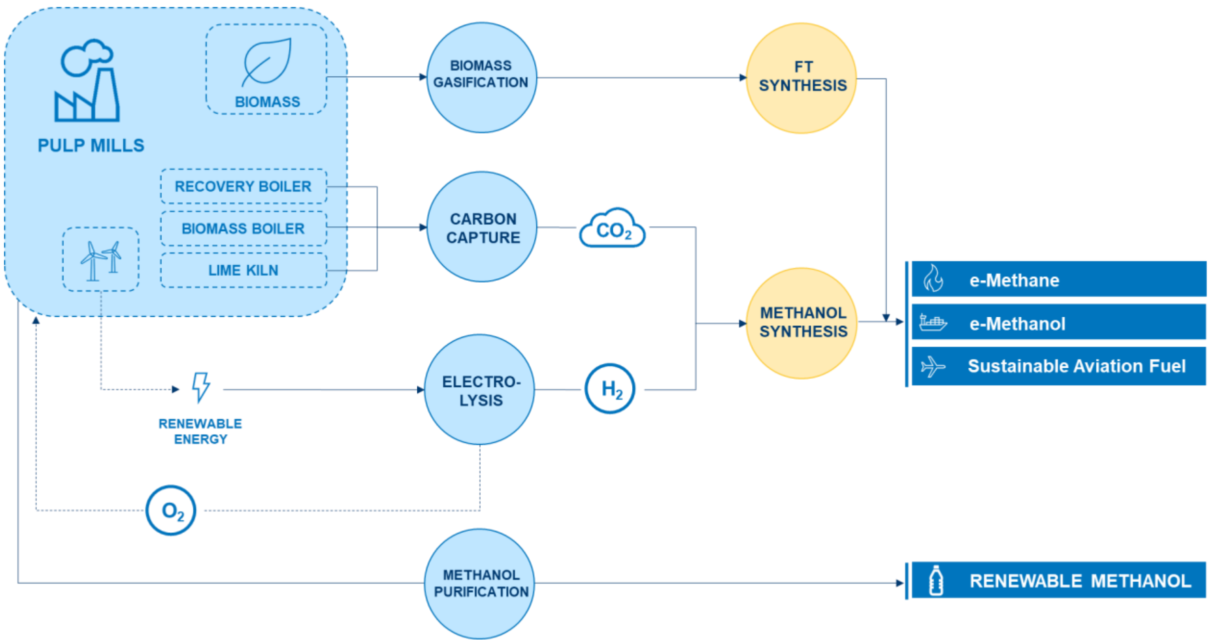


*Figure 2. Integration of new technologies to a pulp mill to create the biorefinery of the future.*

Upgrading the methanol produced in pulping processes with a methanol purification process is a steppingstone for other methanol production pathways. Converting the pulp mill biogenic $CO_2$

emissions into methanol by combining carbon capture, electrolysis, and methanol synthesis to produce e-methanol, can simultaneously be one pathway for decarbonizing the pulp mill. Excess biomass from pulp mills can undergo gasification to produce syngas, which is a raw material for Fischer-Tropsch - synthesis to produce methanol by converting carbon monoxide and hydrogen in the syngas into methanol.

## METHANOL PURIFICATION PROCESS

The methanol purification process can be divided into two processes: light and full purification. The process can be selected according to the required methanol specifications depending on the end-use and customer.

In light purification (Figure 3), the objective is to remove nitrogen, primarily in the form of ammonia ($NH_3$), and easily vaporizing sulfur compounds from raw methanol. The resulting product is known as cleaned or pre-treated methanol. The cleaned methanol is considered an ideal biofuel for recovery boilers or lime kilns because it does not produce $NO_x$ (nitrogen oxides) and $SO_x$ (sulfur oxides) emissions, and its collection for pulp mill utilization is cost-effective.

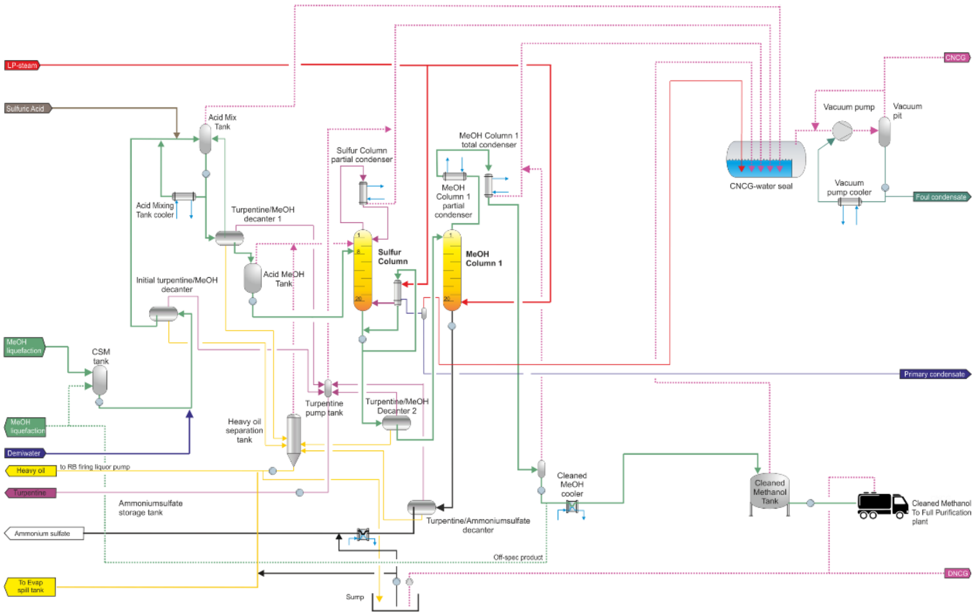

*Figure 3. ANDRITZ light purification process.*

In light purification, raw methanol is acidified using sulphuric acid. Ammonia is then neutralized to form an ammonium sulphate solution. Dilution water is added to maintain solubility. The addition of dilution water reduces the solubility of turpentine compounds in methanol, enabling separation through decantation. In subsequent distillation steps, sulfuric compounds (mainly $H_2S$, MM, and DMS) are distilled from the solution as a light gas fraction, which is then directed to the mill's CNCG system. Methanol is then distilled from the ammonium sulphate-water solution. The resulting intermediate product, known as cleaned methanol, can be used as a biofuel in a recovery boiler or lime kiln.

In full purification (Figure 4), the methanol is further processed to meet the specific requirements of biomethanol, such as IMPCA quality. The full purification process ensures that the methanol product meets the necessary standards for its designated application.

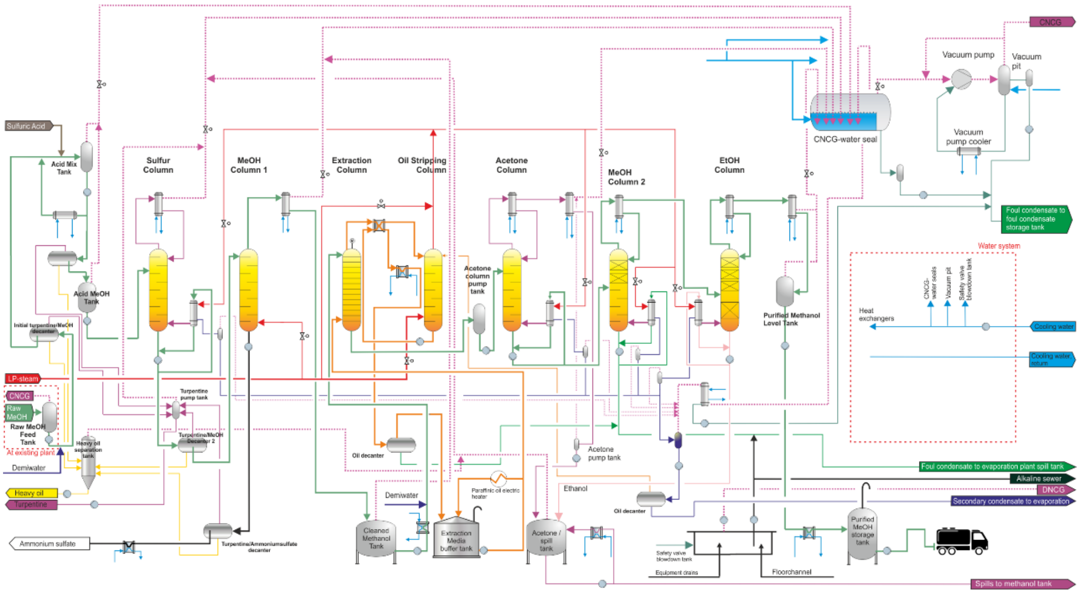

*Figure 4. ANDRITZ full methanol purification process.*

In the full purification process, the cleaned methanol is first fed to an extraction column, which removes impurities that cannot be removed by distillation. The main such impurity is DMDS, but additionally a high variety of other non-polar impurities with low concentration exist. After extraction, the methanol is purified in a series of distillation stages to remove acetone, ethanol, and water in order to finally recover the fully purified methanol.

The methanol purification plant is fully integrated with a pulp mill. Gases generated during the purification process are directed to the CNCG system for further treatment. Condensates produced during the process are routed to the evaporation plant. The ammonium sulphate solution, a by-product of the purification process, is directed to the effluent plant, where it serves as a valuable nutrient for the treatment of effluent microbes.

Any ethanol, acetone, and off-spec methanol that are present in the process are incinerated in the recovery boiler. Recovered turpentine, a by-product of the methanol purification process, is collected and routed to the mill's turpentine collection system. The methanol purification process also contributes to an increased recovery of turpentine in the mill, as the turpentine present in raw methanol is not lost in the recovery boiler.

By converting the methanol from pulp mill processes into high-quality biomethanol, the $CO_2$ emissions are lower compared to fossil-based methanol. The $CO_2$ emissions of biomethanol are negligible compared to the emissions for coal or natural gas -based methanol, which range from 700 to 4500 gCO2eq/kgMeOH. [2]

## CARBON CAPTURE POTENTIAL AND TECHNOLOGIES

The carbon capture potential from pulp mills is substantial and attractive, as majority of the $CO_2$ emissions is biogenic. The biogenic carbon capture potential from a kraft pulp mill is commonly 2.5 – 3.0 tons of $CO_2$/ADt. And as majority of pulp mills are fossil free, as lime kiln can utilize biofuels, approximately 75 – 100% of $CO_2$ emissions are biogenic, which enables recycling of biogenic carbon. [3] Different technologies exist for carbon capture from pulp mill flue gases.

In Figure 5 and Figure 6, two alternatives for carbon capture process are presented. In the amine process (Figure 5) the CO2 rich emission stream, such as flue gas, flows through a pre-scrubber and is then directed to the absorption unit where it flows with the amine solvent counter current. The $CO_2$ rich solvent flows from the bottom of the absorber to the top of the regenerator through a heat exchanger.

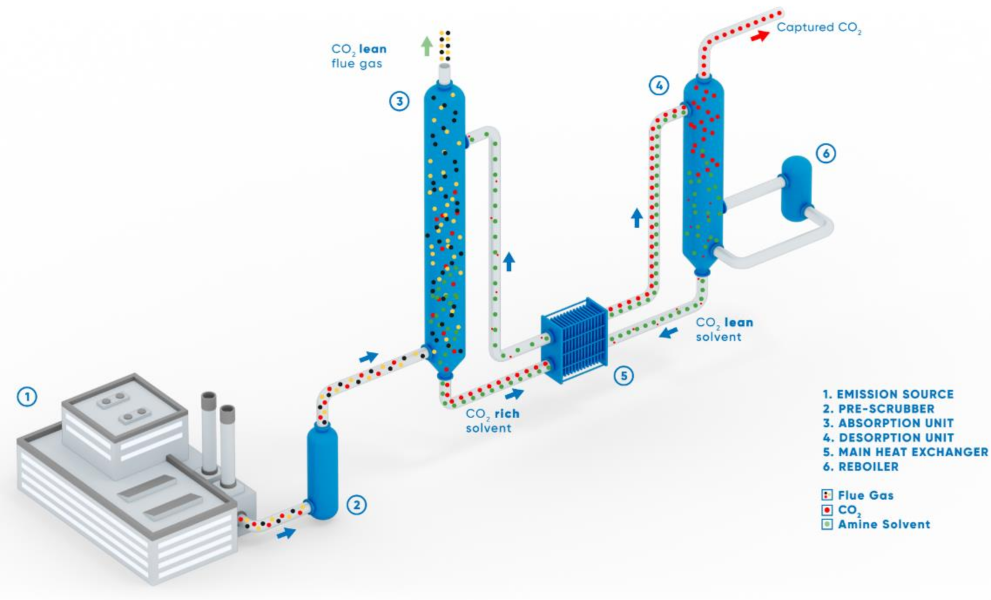


*Figure 5. Carbon capture technology utilizing amine-based solvents and chemical absorption process.*

Subsequently, the flue gas enters the absorption column, where continuous absorption or scrubbing of $CO_2$ occurs using the solvent. This absorption process takes advantage of the reversible chemical reaction between $CO_2$ and the solvent. The resulting $CO_2$ lean flue gas exits the top of the absorber and is directed towards the stack for release. Meanwhile, the $CO_2$ rich solvent is transferred to the desorption unit.

In the desorption unit, a combination of hot solvent from the reboiler and partially fresh solvent enters, initiating the removal or stripping of $CO_2$ from the solvent. Consequently, a pure $CO_2$ stream is collected at the top of the stripper. The $CO_2$ lean solvent is then regenerated and circulated back to the absorption unit for further $CO_2$ capture. The pure $CO_2$ stream undergoes additional processing to achieve the required level of purity before undergoing compression, transportation, or storage for future applications.

Membrane separation process (Figure 6) utilizes the reversible chemical reaction between $CO_2$ and the reactive amine carrier to facilitate the efficient transport of $CO_2$ across the membrane. In contrast, non-reactive components solely rely on the physical solution-diffusion mechanism for membrane transport. Additionally, a high $CO_2$ flux is achieved by connecting the permeate gas to a vacuum, thereby creating a substantial driving force.

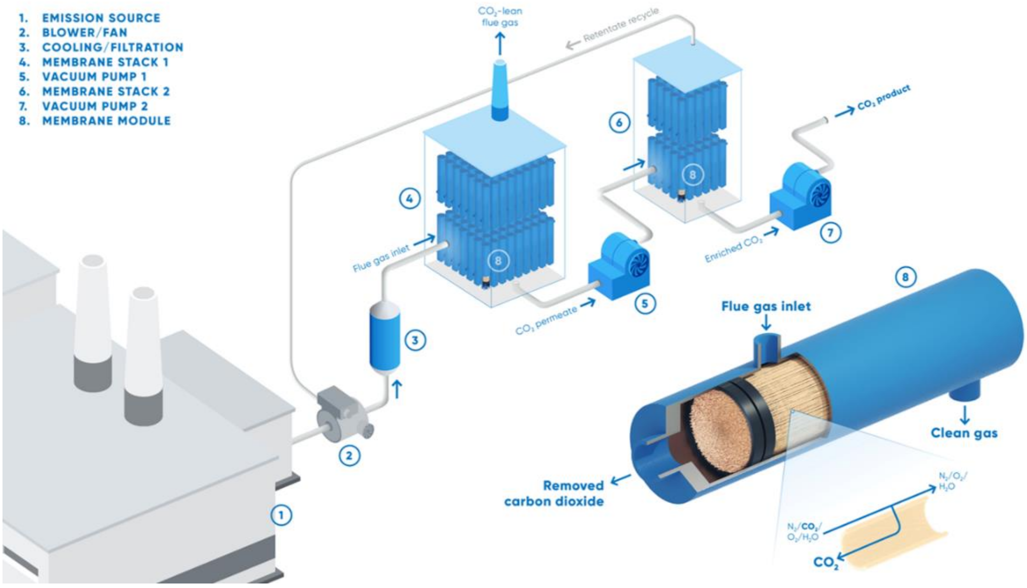


*Figure 6. Membrane separation process for carbon capture.*

Implementing the $CO_2$ capture can benefit pulp mill through multiple routes: the captured $CO_2$ is a raw material for not only e-fuel production but for a variety of bioproducts, such as lignin processes to separate lignin from black liquor or in tall oil manufacturing.

## E-METHANOL PRODUCTION

Due to new investments in renewable energy sources, such as wind and solar, an increasing amount of renewable energy production will emerge in the grid in the upcoming years globally. The Nordics, Western Europe and Latin America will have high shares of renewable energies and they are especially attractive locations for renewable methanol production. [4]

Electrolysis plays a crucial role in e-methanol production: electrolysis is used to split water ($H_2O$) into hydrogen ($H_2$) and oxygen ($O_2$). The hydrogen produced via water electrolysis is combined with captured carbon dioxide to synthesise methanol in methanol synthesis process (1):

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \quad (1)$$

The e-methanol synthesis is a process where the carbon captured carbon is combined with the hydrogen over a catalyst to produce methanol. Alternative pathway for e-methanol, is gasification of biomass to produce syngas which is combined with green hydrogen and MeOH synthesis.

Oxygen is a major by-product from the electrolysis process. Utilizing the excess oxygen in other processes or industries would be beneficial for the concept feasibility. Input of oxygen into pulp mill processes, such as combustion process, might be beneficial. Pulp mills are already major oxygen consumers, and other major industries to utilize oxygen are steel, mining, and chemical industries.

## PATHWAYS TO DECARBONIZE PULP MILLS

Several pathways for decarbonization, or reduction of greenhouse gas emissions, of pulp mills exists. Simultaneously, the decarbonization has a major effect on pulp mill scope 3 emissions. Transitioning from fossil fuels to renewable fuels is a step towards decarbonization. Replacing fossil fuels, such as natural gas in lime kiln or gasoline or diesel in raw material delivery trucks, with renewable methanol helps pulp mills to directly reduce emissions from utilized energy in the manufacturing processes.

## REGULATORY FRAMEWORK

Europe and the US lead the way in e-fuel policies: both have finally implemented policies and initiatives to promote the production and utilization of renewable fuels. These policies create a framework that affects investment decisions in advanced biofuels and RFNBOs.

The European Union, through policies like RED III, has set specific targets for the use of advanced biofuels and RFNBOs. By 2030, there is a minimum requirement of 8.9 Mtoe/a of advanced biofuel or RFNBOs. The policies also include regulations on renewable electricity, $CO_2$ capture, and greenhouse gas emission calculations [5].

US policies provide support for hydrogen production and carbon capture, enabling the export of RFNBOs to the European market. Generous tax credits in the US can decrease the costs associated with hydrogen and $CO_2$ production. However, support for the consumption of advanced fuels in the US is limited, as the transportation sector can fulfill its obligations using low-cost crop biofuels.

The EU has separate targets for sustainable aviation fuel (SAF) and RFNBOs in the aviation sector (Refuel Aviation). This creates a strong driver for the development of Fischer-Tropsch and Methanol-to-Jet technologies. In the maritime sector (FuelEU Maritime), there is a requirement for a minimum 6% greenhouse gas reduction in energy use, without a specific RFNBO target. [5]

The policies and targets for e-fuels can have implications for pulp mills, as they may consider investing in advanced biofuel production or RFNBO technologies to meet the increasing demand. The availability of generous tax credits in the US can influence investment decisions regarding hydrogen and $CO_2$.

## SUMMARY

Pulp mills can play a significant role in meeting the demand for renewable chemicals and biofuels. Methanol is already produced as a by-product in pulp mills, and by refining it further, high-quality biomethanol can be obtained, serving as an important raw material for various industries.

The purification process removes impurities, resulting in purified methanol suitable for different applications. Carbon capture technologies can be employed to utilize $CO_2$ emissions from pulp mills, converting them into valuable methanol using hydrogen produced through water electrolysis in methanol synthesis. The regulatory framework, with emphasis on the EU and US policies, support the production of advanced biofuels and RFNBOs. Tax credits in the US can significantly reduce production costs. The overall aim is to establish pulp mills as biorefineries, contributing to a more sustainable and circular economy.

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