Converting Waste Gases from Pulp Mills into Value-Added Chemicals

Tom L. Burgess,[a] Andrew G. Gibson,[b] Saul J. Furstein,[c] and Israel E. Wachs[d]
[a] Tom Burgess Consulting, Ltd., 1376 Gabriola Drive, Parksville, B.C., V9P 2T5, Canada. Retired from Georgia-Pacific
[b] Gibson Technologies Inc., 2293 Little Brooke Trace, Atlanta, GA 30338
[c] Georgia-Pacific Corporation, 133 Peachtree Street, N.E., Atlanta, GA 30303
[d] Lehigh University, Chemical Engineering Dept., Iacocca Hall, 111 Research Drive, Bethlehem, PA 18015-4791

A combined sorption/catalytic process has been discovered that converts the methanol and mercaptans in Kraft pulp mill waste gas condensates into formaldehyde. A pilot plant was operated at Georgia-Pacific's Brunswick, GA, mill for two years to optimize both sorbents and catalyst. Patents were issued. Applications within Georgia-Pacific and external licensing opportunities for the process are being investigated. The process gives pulp and paper mills a profitable alternative for converting their waste gases to valuable chemicals, as opposed to incineration or biodegradation in treatment ponds.

INTRODUCTION

Methanol is the largest single source of volatile organic compound (VOC) emissions from Kraft pulp mills, accounting for 70 to 80% of total emissions. The methanol is formed during the pulping of wood and is contaminated with reduced sulfur compounds and terpenes. The Cluster Rule [1], which went into effect April 15, 2001, places limits on methanol emissions for all pulp mills in the U.S. Canada faces similar legislation. Approximately 150 mills are affected in North America. In addition, about another 300 mills offshore have the same emission levels.

Methanol emissions can be reduced by collecting condensate streams from the digesters, evaporators, and other sources in the mill. The collected condensate streams can then be steam-stripped to concentrate the methanol for incineration. A few mills are "hard-piped" to send this methanol-laden stream to bio-treatment ponds, thus avoiding incineration. It was estimated that, by the end of 2001, about 70% of the Kraft pulp mills in the United States would have stripping units for this purpose.

Stripper overhead gas (SOG) comprises more than methanol. Other components include:

Component	Weight %
Methanol	40 - 50%
Water	40 - 50%
Total Reduced Sulfur (TRS)	1 - 5%
Terpenes	1 - 5%

In most cases in the U.S., the SOG will likely go to an incinerator, kiln, or boiler where the mixture is burned. But, there are frequently flameout problems at the incinerator, due to the low fuel value of this stream. This outage can result in permit violations due to emission of the unburned gases. To minimize flameouts, natural gas is often needed as a supplemental fuel, with an attendant increase in fuel cost.

Recently, some mills have found it advantageous to rectify the SOG to about 80% methanol and collect it as a liquid. This liquid methanol has a higher fuel value, thereby reducing the amount of natural gas that has to be purchased and reducing the chance of flameouts.

The availability of this *concentrated* (70-80%) methanol stream can allow an alternative to using it as a fuel. A process has been developed at Georgia-Pacific that converts the methanol and TRS (mostly mercaptans) in the rectified SOG into formaldehyde. Based on work done by Professor Israel Wachs of the Chemical Engineering Department of Lehigh University in Bethlehem, PA, this patented catalytic process [2, 3] has achieved commercially viable yields of formaldehyde (70-80%) from a typical pulp mill SOG feedstock containing methanol, water, and TRS compounds.

The process presents Kraft mills with a more profitable alternative for SOG than incinerating it as a fuel. The formaldehyde produced can be used by resin manufacturers to produce thermosetting resins commonly used in plywood and other structural panels. A typical pulp mill of 2,000 ADTPD (Air-Dried Tons Per Day) output may achieve a payout of 2 to 4 years, depending on the price of methanol and local economics.

The process also produces two levels of low-pressure steam, 60 and 150 psig, usable within a paper mill, and reduces the generation of greenhouse gases because the methanol is largely converted to formaldehyde, rather than CO_2. The reduction in CO_2 emissions is about 80-85% of the amount otherwise generated by incineration. For a 2000 APTPD mill, this equates to 28 tons per year of CO_2 emissions that are avoided.

PROCESS DEVELOPMENT BACKGROUND

Catalyst Development

At the heart of the process is the catalyst that converts methanol to formaldehyde in the presence of TRS compounds, and the large amounts of water vapor present in SOG. Existing formaldehyde catalysts that use pure commercial-grade methanol are "bulk" metal oxides or metallic silver. The bulk metal oxides are unstable and deteriorate in the presence of steam, and deactivate in the presence of TRS compounds. The metallic silver catalyst also deactivates in the presence of sulfur (the familiar silver "tarnish" reaction). The catalyst used in this new process is a "supported" metal oxide catalyst (vanadium pentoxide on titania support) that has proven to be more stable under the demanding conditions imposed by an SOG stream. As shown in Figure 1, a typical mercaptan, dimethyl sulfide, is converted to formaldehyde by this catalyst at temperatures above 350° C. Similar reactions are seen with many other mercaptans, most of which are present in SOG. The methanol in the SOG is converted by this same catalyst in yields of 70-80%. The main by-product is CO, as indicated in the side reaction (2) shown below. This reaction also contributes undesired amounts of water dilution to the final product, which is a 50% solution. Unlike existing commercial formaldehyde catalysts, the new catalyst is not deactivated, either by large amounts of water or by sulfur (TRS) compounds.

The reactions that occur are as follows:

Desired Reaction

$$CH_3OH + 1/2\ O_2 \rightarrow HCHO + H_2O \qquad (1)$$

Catalyst, 320° C

Side Reaction

$$HCHO + 1/2\ O_2 \rightarrow CO + H_2O \qquad (2)$$

Catalyst, > 350° C

Mercaptan Reaction

$$CH_3SH + 2\ O_2 \rightarrow HCHO + SO_2 + H_2O \qquad (3)$$

Catalyst, 320° C

Three aspects of this process are novel:

1. The methanol-to-formaldehyde reaction catalyst is not poisoned by the sulfurous compounds present as would be the case if commercial formaldehyde catalysts were used.
2. The same catalyst *simultaneously* converts mercaptans to formaldehyde
3. There is no potentially corrosive SO_3 produced. This is important because the product is absorbed in water and shipped as a 50% water solution.

Several other important environmental aspects were noted for this process during these initial operations. Significant amounts of NH_3 (as much as 1-3%) present in the SOG were completely reacted to nitrogen. There was no NH_3 in the process vent from the reactor. Secondly, no NO_x compounds were seen in the reactor vent, which is usually the case when SOG is incinerated. (A recent TAPPI paper [4] illustrates the difficulties encountered with NO_x formation when SOG is incinerated.) Finally, the absolute amount of SO_2 in the reactor vent, while no different than that released during incineration, is in a more concentrated form, thereby permitting its use as a recycle stream to the digesters. It can be transmitted as a dilute gas, or liquified for transport within the mill. These three advantages can impact favorably in situations where emission limits are becoming restrictive.

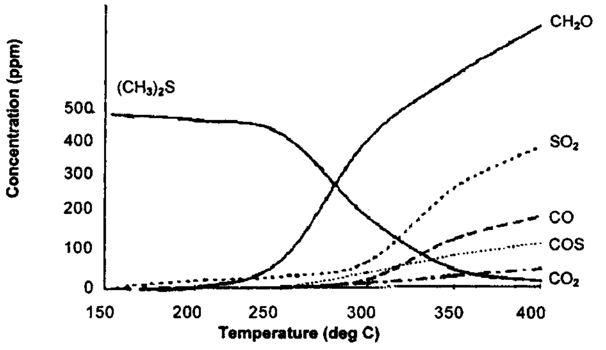

Figure 1. Dimethyl sulfide oxidation at Georgia-Pacific Corporation.

Sorption Step

While the new catalyst formed the heart of the process, a successful pilot operation was not achieved until an important sorption step was developed. This addressed the terpenes present in SOG. It was impractical to test the effect of terpenes in the micro-reactors at Lehigh University, where the partial oxidation catalyst for methanol and mercaptans was developed. Consequently, the first exposure of the new catalyst to terpenes happened in the pilot plant discussed below and shown schematically in Figure 2. Deactivation of the catalyst due to terpenes occurred within a few hours of operation, using as feedstock a slipstream of pulp mill SOG. Although not present in large concentrations, the terpenes, mostly 10-carbon atom compounds, "smothered" the active reaction sites and blocked the single-carbon methanol and mercaptan molecules from access.

The need for a feed purification step to remove terpenes was thus identified, and various sorption technologies were tested, among them molecular sieves and other sorption resins. The most successful technology proved to be activated carbon, as illustrated in Figure 3. This dramatically shows the comparison of no carbon vs. two types of activated carbon. The Norit carbon was selected for this application because it had a longer onstream time than the Columbia grade. Installation of beds with this type allowed the reactor to stay on line for the required periods of time, and permitted the experiments for the pilot plant to proceed as planned.

During its two-year operation at Georgia-Pacific's Brunswick, GA, pulp mill, the pilot reactor was used to test catalyst formulations, process conditions, feedstream purification steps and product purification steps. The results verified that high amounts of water (40-50 vol. %) were tolerated and that mercaptans (as well as methanol) were converted to formaldehyde. In addition, the process produced commercial-level yields of formaldehyde. The optimum catalyst formulation was also determined because the bench-scale catalysts

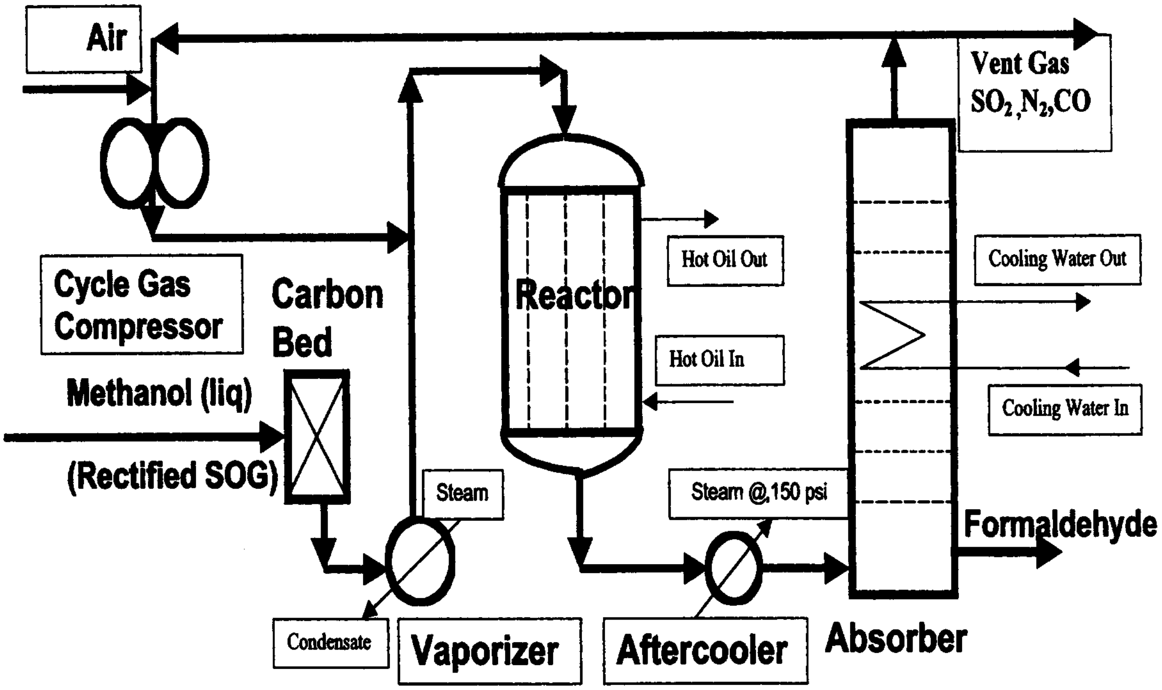

Figure 2. SOG-to-formaldehyde process flow at Georgia-Pacific Corporation pilot plant.

developed at Lehigh were scaled up to commercial catalyst production equipment for the first time by the supplier. The ability of the selected carbon to remove terpenes was also confirmed, but regeneration procedures were not attempted due to other program priorities. Process definition work remains on the sorption step to determine best sorbent available, regeneration cycles, etc.

DESCRIPTION OF PROCESS

The pilot reactor is similar to the pilot plant reactors used for commercial formaldehyde process/catalyst studies. A one inch diameter, stainless steel tube, five feet long, was filled with catalyst pellets and cooled by Dowtherm circulating through a surrounding jacket. Commercial-scale reactors consist of 3,000 to 20,000 such tubes housed in one shell through which Dowtherm is circulated.

As shown in the simplified flow diagram in Figure 2, the 80% methanol stream from a SOG rectifier is pretreated in a carbon bed to remove "heavy compounds," for example terpenes, and then is fed to a vaporizer. The entire process operates at near-atmospheric pressure (0-10 psig). The vaporized feed, at 200° C, flows to the vertical tube-and-shell reactor where it contacts catalyst in the tubes that converts the methanol and mercaptans to formaldehyde. TRS compounds other than mercaptans (for example, H_2S) are converted to SO_2 as well as the sulfur component of the mercaptans. Since the reactions are partial oxidation reactions, air (oxygen) is introduced in the required amounts and blended with the vaporized feed prior to contacting the catalyst. Typical operating parameters were as follows:

INLET GAS	
Oxygen Concentration, vol %	9-10%
Methanol Concentration, vol %	7-9%
Space Velocity, sec $^{(-1)}$	1-1.4
PRODUCT STREAM	
Formaldehyde Concentration, wt %	47% (Note 1)
Methanol Content, %	< 1%
Acidity, %	< 0.3% (Note 2)
REACTION TEMPERATURE	340-360° C
REACTOR PRESSURE	0.5-10 psig

Note 1: The pilot absorber was not designed to "shed" water from the process. A large plant would have this feature because the amounts of water in SOG feedstock, plus the amount formed in the reaction (1 mol of water per mol of formaldehyde), equates to more than the desired 50% concentration for the final product

Note 2: Acidity greater than 0.1% is caused by formic acid formation and in commercial plants is removed by ion exchange. The pilot unit had only batch-type ion exchange facilities capable of reaching 0.3% acidity levels.

The exit gases from the tube-and-shell converter emerge at 350° C, and are partially-cooled in a heat exchanger where 150 psig steam is generated (in full-scale plants). This partially-cooled stream is then fed to a countercurrent absorber which absorbs the formaldehyde gas in water. Because most commercial formaldehyde is sold as a 50% solution, the absorber is operated to approach this concentration as closely as possible.

The SO_2 formed in the reaction is vented from the top of the absorber along with nitrogen, unused oxygen, CO,

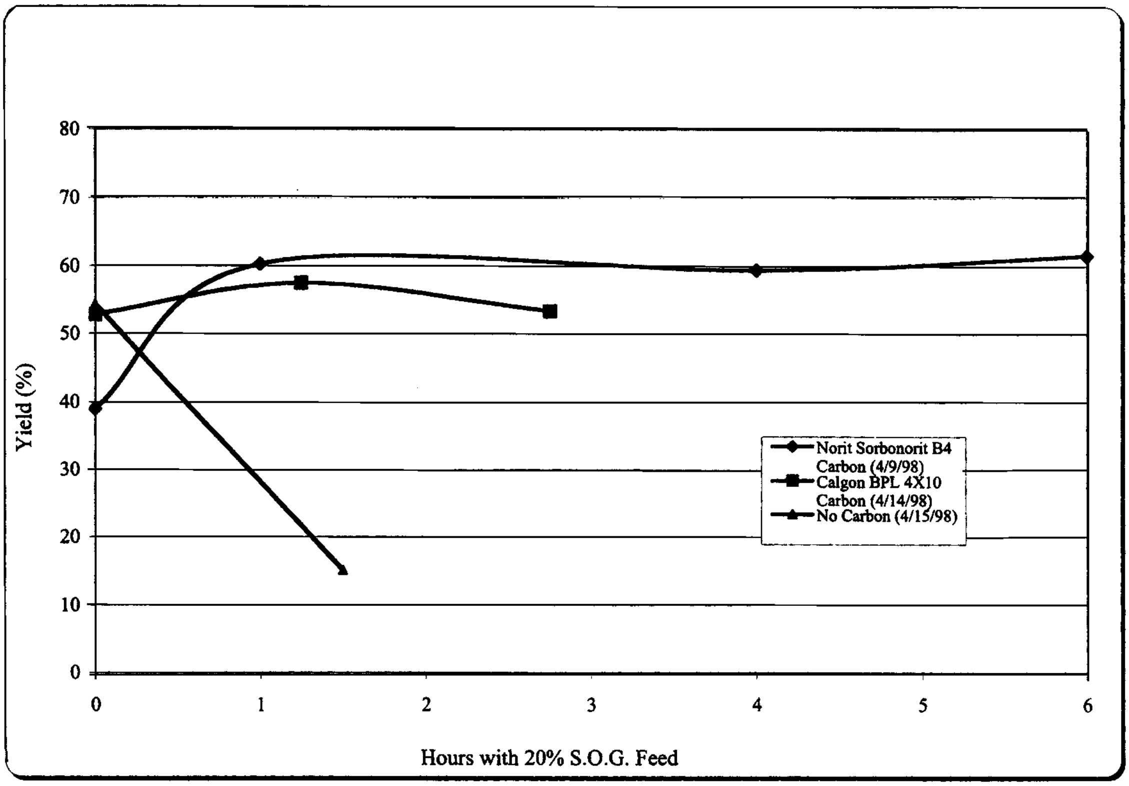

Figure 3. Formaldehyde yields (by difference) vs. hours of reactor operation.

and small amounts of CO_2, the carbon oxides being by-products of the reaction. Some of the absorber offgas is recycled to the converter after make-up oxygen (air) is introduced. This is done to keep oxygen/methanol/mercaptan mixtures below the explosive limit

The reaction is highly exothermic (10 kcal/mol). It is cooled by a heat-transfer medium (Dowtherm) on the shell side of the reactor. With heat exchangers, the outlet Dowtherm stream containing the heat of reaction is cooled by producing low-pressure steam (30-60 psig).

The formaldehyde product is treated to reduce acidity to commercial levels. It can then be transported in conventional tank trucks or railcars to consumers.

SCALE OF OPERATION

For a 2,000 ADTPD pulp mill that captures 14 pounds of methanol per ADT of pulp, a formaldehyde production of 15 million pounds per year (50% concentration basis) is expected. The "footprint" of the plant is 60 ft by 60 ft, exclusive of storage tanks. The 80 ft absorber is the tallest vessel. The plant could be built off the mill site as skid-mounted modules, brought to the mill, and connected.

ECONOMICS

A typical itemization of income, costs and earnings is given in Table 1. For the mill referred to above, a payout period of three to four years is calculated based on formaldehyde prices of $0.06/lb (50%) basis. This assumes a customer-shipping radius of 500 miles from the mill producing the formaldehyde. A heat value credit to the mill is included (equivalent to natural gas fuel) for the methanol that would otherwise have been incinerated and used to generate steam via heat recovery exchangers. If the mill now incinerates without any heat recovery, then this credit to the mill would not apply and the economics would be slightly improved.

Whereas incineration is an environmental cost to the mill, this technology produces a positive income stream, while also eliminating a methanol/TRS emission source. Each mill's economics will vary depending on proximity to a formaldehyde customer, SOG composition, fuel costs, labor costs, etc.

With respect to commercialization, certain economic factors must apply. In any world location, the cost differential between methanol and natural gas is the economic driving force for the project. When this differential is equivalent to the cost factors used for methanol raw material charged to existing formaldehyde processes, e.g., 60 cents per U.S. gallon, and natural gas @ $2.25 per million Btu, (the credit for methanol waste gas incinerated) then the payouts will be 2 to 4 years. This assumes a consuming source for the formaldehyde product within a reasonable shipping radius, that is, 500 miles or less.

A conceptual design of a commercial-scale plant using the new process has been completed. U.S. patents 5,907,066 and 5,969,191 have been issued for the process.

Table 1. Annualized income, costs, and earnings. 2,000 ADTPD mill, 14 lb methanol/ton in SOG.

Income 15,000,000 lb/yr formaldehyde (50%) @ $0.06/lb, FOB mill	$900,000
Operating Cost	
Direct Labor	$110,000
Utilities	$25,000
Methanol in feed @ $2.25/MMBTU fuel value *	$260,000
Misc., catalyst, supplies, etc	$70,000
TOTAL OPERATING COST	$465,000
Gross Margin	$435,000
Depreciation	$210,000
EARNINGS BEFORE TAX	$225,000
Credit for Steam Generated (depending on mill steam balance)	$95,000
Credit for Terpenes Recovered and Sold	$110,000
Credit for SO_2 Recycled	$ 45,000
TOTAL BYPRODUCT CREDITS	$250,000
TOTAL EARNINGS, INCLUDING BYPRODUCT CREDITS	$475,000

* This cost applies only if mill currently has heat recovery on the incinerator.

CONCLUSIONS

The objective of the project was to develop a process that can produce a valuable chemical, formaldehyde, from a waste stream, Stripper Overhead Gas. This has been successfully demonstrated on a pilot-scale.

The approach used in this project may be useful in treating other emission mixtures containing reactive chemicals. It focused on developing a catalyst that would function in the presence of contaminants that were chemically similar in structure to the main ingredient, methanol. The mercaptan contaminants were similar in structure and molecular size and did respond to the catalyst in the same manner as methanol.

Heavy terpenes were an obstacle to the operation and we expected them to be sufficiently removed by rectification. This was not the case. Terpenes behaved in the distillation column much like aerosols. They simply passed up through the rectification stages and fractional percentages appeared in the distilled SOG. Thus, it's necessary to remove them by other means, such as sorption, so that the catalyst would not be deactivated. As shown in the table above, terpenes recovered from carbon bed regeneration (with steam) can produce additional revenue

We believe the disappearance of ammonia occurs via a chemical pathway wherein the ammonia is first oxidized to NO_X over the catalyst, and then is reduced to molecular nitrogen and water by the hydrogen present in the reactor as a result of the methoxy formation at the catalyst site releasing reactive hydrogen. The mass ratio of such hydrogen to the NO_X formed from the ammonia is much greater than those used in conventional selective catalytic reduction (SCR) reactors employed for NO_X removal. Such a reducing atmosphere favors NO_X reduction This process exhibited no ammonia "slip," or non-conversion, such as that seen from incinerators.

There may be other cases where a promising environmental catalyst failed because of poisoning. In such instances, feedstream purification techniques aimed at selective removal may provide an answer. One such example is low pressure polyolefin catalysts, where as many as seven feedstream purification steps in series have been used.

Georgia-Pacific is now considering licensing the technology.

ACKNOWLEDGMENTS

The authors thank all the people at Georgia-Pacific who contributed their time and efforts to the success of this project.

Special recognition is given to Professor Israel E. Wachs for literally "designing a catalyst" in response to a pressing environmental requirement.

LITERATURE CITED

1. Cluster Rule Regulation: 40CFR Part 63, Subpart S (foul condensates), Section 63.446.
2. **Wachs, Israel E.**, Lehigh University, Bethlehem, PA, U.S. Patent 5,907,066, "Treating Methanol-Containing Waste Gas Streams," May 25, 1999.
3. **Wachs, Israel E.**, Lehigh University, Bethlehem, PA, U.S. Patent 5,969,191, "Production of Formaldehyde from Methyl Mercaptans," October 19, 1999.
4. **Crawford, Robert J. and Ashok K. Jain,** "Effect of Stripper Off-Gas Burning on NOx Emissions," *Solutions*, TAPPI and PIMA, NCASI, PO Box 141020, Gainesville, FL 32614-1020, January 2002.