PROCESS SIMULATION

Millwide methanol balances: Predicting and evaluating HAP emissions by utilizing process simulation techniques

VENKI VENKATESH, WILBERT L. LAPP, AND JERRY L. PARR

ABSTRACT

For the purposes of Title V air permitting and Cluster Rule planning, a comprehensive methanol and HAP sampling program of major process streams and emission sources has been conducted at Mead's integrated pulp and paper mills. Process modeling is a useful tool to systematize this information for "benchmarking" current operations and in evaluating alternatives. Methanol loading in key effluent, internal process streams, and emission sources has been predicted from millwide models using process simulation. The accuracy of the simulation is established by cross-checking against measured mill data. Actual case studies are discussed, showing methanol modeling is a valid technique to evaluate HAP control process alternatives.

Application:

Information presented in this paper can be used by mills to evaluate process alternatives and their impact on HAP emissions.

As part of the planning for the EPA's Title V air permit and proposed Cluster Rule standards, a comprehensive sampling program for methanol and other hazardous air pollutants (HAPs) from major process streams and emission sources has been undertaken at many pulp and paper mills. Methanol/HAP release from mill process vents is a function of the methanol content of the associated process stream and is influenced by condensate reuse practices at the mill. Compliance can impose a large capital burden on mills if standard noncondensable gases (NCG) collection, condensate segregation, and methanol steam stripping technologies widely used since the late 1970s were uncritically applied to all methanol/HAP sources. Consequently, there is significant industry interest in improved quantification of methanol and HAP loading and their distribution in mill streams.

Methanol is generated from the methoxyl groups present in lignin and hemicellulose during cooking in the digester *(1, 2)*. Methanol generation is favored by high digester pH, high alkali charge, high cooking temperature, and long cooking times. Methanol generation also depends on the pulping process, and **Table I** shows that Mead data correspond well with the published data. The manner in which methanol distributes in mill streams is impacted by process configuration and condensate reuse practices. Application of process simulation offers:

- An approach to track the distribution of methanol in different mill streams
- The ability to normalize large mill emission databases in a more manageable form.

This paper summarizes the results of process simulation studies conducted at two Mead mills to benchmark current operations and evaluate alternatives to ensure reduced loading in compliance with the anticipated standards.

PROCESS SIMULATION

The general energy and materials balance system (GEMS) process simulator, widely used in pulp and paper mill simulation since the 1970s, has been used to predict methanol concentrations in pulp mill streams. The prediction capability was added to GEMS by incorporating methanol vapor–liquid equilibrium data from published data *(1–9)* and other sources. Since methanol simulation is a new application, the predictions have been verified by comparison with mill and lab pulping studies presented here and with other sources *(1–11)*.

Application of simulation permits a systematic evaluation of HAP data that were generated from Mead's extensive sampling programs. Overall model predictions have been substantiated by mill experience at Mead and those reported in the literature:

- Methanol is distributed differently than kraft odor compounds in mill process streams. Methanol is retained more in black liquor and condensate streams in preference to being vaporized.
- Methanol (currently classified as a HAP) can be used to track other HAPs, such as methyl ethyl ketone and acetaldehyde.
- Methanol that is formed during cooking and in batch digester plants is typically distributed as follows: (a) 45–60% is split off with the relief and blow gases, (b) 30–40% goes with weak black liquor to evaporators, and (c) 10–15% goes with the brownstock.

Source	Methanol, lb/a.d. ton
Mill A	19.0
Mead Research	
Hardwood	20.0–21.7
Softwood	20.0–21.0
Mill B (lb/o.d. ton)	3.93
Mill C	20.4
Mill D	21.6
Mill E	19.0
NCASI (1995, 15 mills)	21.1
Finland (1977)	
Batch softwood (5 mills)	19.1
Continuous softwood (2 mills)	19.5
Batch hardwood	22.0

*All alkaline except Mill B, which is semichemical

*I. Methanol generation comparison**

Fiberline stream	Mill data	Model calculations
Heat recovery water:		
MeOH, ppm	548	520
Brownstock washer feed:		
MeOH, ppm	506	500
Weak black liquor:		
Solids, %	15.5	15.2
MeOH, ppm	481	476
Brownstock to screen room:		
Consistency, %	12.0–12.5	12.5
MeOH, ppm	402	430
Decker overflow:		
MeOH, ppm	180	200
Stock to bleach plant:		
Consistency, %	12.0	12.0
MeOH, ppm	196	200

II. Mill A: Methanol balance—A comparison of mill data with model calculations

Process simulation applications

Two mill simulation applications are discussed in this paper. In both cases, existing GEMS process models of the fiberline and liquor cycle were modified to include methanol prediction capability.

- **Mill A:** The mill has batch digesters followed by three stages of washing, open screening, and a decker. Blow heat capacity is limited, and blow/relief condensates are reused as brownstock shower water. Weak black liquor is concentrated in a five-effect evaporator followed by concentrators. The simulation study was conducted to evaluate lower-cost process alternatives to steam stripping.
- **Mill B**: This semichemical pulp mill has a continuous digester followed by three pressure washers and refining. Digester blow and evaporator condensates are used as brownstock shower water. Weak liquor at 9–10% is concentrated in a five-effect evaporator followed by a concentrator. The simulation study was conducted to evaluate the methanol/HAP emission impact of planned process modifications.

Process simulation—Mill A: Model validation. **Tables II and III** show that the GEMS calculations of methanol concentration correspond well with the mill stream concentration data, thus validating the simulation. **Table IV** shows methanol loading in different mill streams computed from the GEMS model. Air emissions in the model are established by difference from the aqueous stream loading data.

The following conclusions are noted from the model projections.

Digester area: Blow heat recovery.

The total methanol generated during cooking is 19 lb/a.d. ton, of which air emissions from the fiberline area were estimated to be 7.7 lb/a.d. ton (Table IV).

Digester area emissions, estimated at 0.63 lb/a.d. ton, accounted for 6–10% of the methanol in the blow/relief gases going to the blow heat recovery system. The model indicated that this methanol was present in 17–20% of the blow vapors that remained uncondensed due to equipment limitations.

The methanol entering with the weak liquor in the blow-tank stock is not a major contributor to washer hood emissions. Use of methanol containing heat recovery water in the brownstock washer showers was found to be the major contributor to the methanol air emissions from the washer hoods and from the

"open" screen room equipment.

About half the methanol in the heat recovery water used on the brownstock washer showers is released at the washer hoods (4 lb/a.d. ton). NCASI's survey *(9)* shows methanol emissions of 0.09–2.28 lb/a.d. ton. Hood emission at Mill A is higher because of the high methanol content (520 ppm) in the shower water.

Some 50% of the methanol in the third washer stock is released as air emissions in the screen room (3 lb/a.d. ton). About 3.0 lb/a.d. ton methanol are carried over to the bleach plant.

Evaporators: Methanol segregation in condensates.

Table V shows the current levels of methanol segregation (i.e., achieving high methanol concentration in a low-flow "contaminated" evaporator condensate) in the evaporators. As would be expected for evaporators that were not designed for control of kraft odors, methanol segregation is difficult to accomplish in older equipment.

Forty-six percent of the methanol present in the weak liquor is segregated in the contaminated condensate, which represents 21% of the total condensate flow. This contaminated condensate stream is the only mill effluent with a methanol concentration above 1000 ppm.

The evaporator hotwell, typically a major source of NCG odor gases in kraft mills, has only 2.8% of the entering methanol at Mill A at a concentration of less than 100 ppm. This translates to a maximum possible emission of only 0.2 lb/a.d. ton.

Mill A: Process alternatives to reduce methanol release. Process modifications considered to reduce methanol release to the atmosphere are noted below. The thrust of the alternatives was to achieve greater levels of methanol segregation in select condensate streams and to minimize the need for expensive steam stripping. Each alternative was evaluated using the Mill A GEMS model.

A list of alternatives is as follows:

1. Modified and expanded blow

	METHANOL CONCENTRATION, PPM	
Evaporator condensate	**Mill data (avg.)**	**Model calculations**
Clean condensate	577	578
Contaminated condensate	1321	1312
Hotwell condensate	80	90

III. Mill A: Methanol balance—A comparison of mill data with model calculations

Source	Current	Modified blow heat rec.	Modified blow heat & closed screen
Generation	19.0	19.0	19.0
Emissions:			
Uncondensed blow/relief	0.63	N/A*	N/A
Washer hood vents	4.04	0.05	0.80
Screen room release	3.0	1.57	0
Evaporator hotwell	0.02	0.02	0.02
Sec. condenser vent	N/A	0.30	0.30
Total:	7.69	1.94	1.12
Stream loads:			
Accumulator overflow	N/A	3.6	3.6
Sec. condenser	N/A	6.36	6.36
Evap. clean condensate	4.23	3.0	3.2
Evap. contaminated cond.	4.02	2.36	2.6
Ejector condensate	0.10	0.10	0.10
Concentrator hotwell	0.10	0.10	0.10
Screen room sewer	0.04	0.02	0.06
Decker overflow, Misc.	0.05	0.04	N/A
Carryover to bleach plant	3.00	1.40	1.80

*Not applicable

IV. Mill A: Simulation results (alternative 1)—Methanol loading, lb/a.d. ton

Stream	FLOW, % total flow	METHANOL ppm	LEVEL % total
Clean condensate	48.7	578	50.0
Contaminated condensate	21	1312	46.0
Ejector condensates	15	90	2.8
Concentrator condensate	15.3	31	1.2

V. Mill A condensate segregation: Evaporator condensate streams

Source	Current	Modified blow heat rec.	Modified blow heat & closed screen
Stream:			
Heat recovery water (reused)	520	N/A*	N/A
Accumulator overflow	N/A	1,567	1,567
Sec. condenser condensate	N/A	10,240	10,240
Evap. clean condensate	578	404	430
Evap. contaminated cond.	1,312	758	830
Ejector condensate	90	60	60
Concentrator hotwell	31	22	22
Screen room sewer	200	100	300

*Not applicable

VI. Mill A: Simulation results (alternative 1)—Methanol stream concentrations, ppm

Condensate segregation	Current MeOH, ppm	Modified blow heat recovery & pre-evaporator MeOH, ppm
Sec. condenser condensate	N/A*	9360
Accumulator underflow	N/A	1244
Pre-evaporator condensate (combined)	N/A	1586
Clean condensate	578	148
Contaminated condensate	1312	278
Evap. ejector condensates	90	20
Concentrator condensate	31	10

*Not applicable

VII. Mill A: Simulation results (alternative 2)—Impact of pre-evaporator (two-effect)

heat recovery system with condensate segregation and (a) current screen room and (b) pressure screens and decker/screen room closure
2. Modified and expanded blow heat recovery system with two-effect pre-evaporators
3. Modified and expanded blow heat recovery system with steam stripping of select streams: (a) blow condensates only, (b) blow and evaporator condensates, and (c) blow and select evaporator condensates.

Simulation results are presented in **Tables IV, VI, and VII**. Note that upgrading the digester blow heat recovery system [alternative 1(a)] will accomplish the following:

- Reduce fiberline area methanol emissions by 75% from 7.7 to 1.94 lb/a.d. ton
- Produce two digester condensate streams containing 9.96 lb/a.d. ton of methanol (52% of total) at concentration levels above 1000 ppm
- Reduce methanol concentration to 760 ppm in the contaminated evaporator condensate from the current 1300 ppm (Table VI).

In alternative 1(b), replacing the current "open" screens with enclosed pressure screens in the screen room and implementing decker/screen room water closure could further reduce screen room emissions. This technology is standard practice in modern kraft mills. This modification, combined with blow heat recovery modifications, is estimated to reduce pulp mill area emissions by 85%, from 7.7 to 1.12 lb/a.d. ton of methanol. However, the combined condensate methanol level increases to 830 ppm.

Alternative 2 explored combining alternative 1(b) with improved condensate segregation by adding a two-effect pre-evaporator (Table VII). Significant methanol segregation is achieved but at high capital costs.

The pre-evaporator condensate streams contain 13.7 lb/a.d. ton methanol (72% of total). The combined evaporator condensate methanol concentration is less than 300 ppm, making possible its reuse.

Alternative 3 examined steam stripping to remove methanol from select contaminated digester options and evaporator condensates (**Table VIII**). Due to the difficulty in achieving methanol segregation in the mill's condensate streams, even a relatively large stripper will accomplish only modest levels of methanol removal in the 40–60% range. Modern mills achieve comparable removal with smaller strippers. The option of piping the more-methanol-rich condensates to the wastewater treatment plant requires less capital and energy.

Mill B: Process simulation. Mill B is a semichemical pulp mill evalu-

KEYWORDS
Air pollution, alcohols, computer programs, emission, hazardous materials, materials balance, methanol, pollution, pollution control, regulations, simulation.

ated for impact of process modifications on methanol and HAP emissions. An existing GEMS model of the mill described elsewhere *(12)* was modified to include methanol predictions. **Table IX** shows good correlation between mill data and predictions.

A methanol generation of 3.93 lb/o.d. ton was predicted for the semichemical process (as already shown in Table I), which is much lower than the 20–21 lb/a.d. ton typical for kraft cooking.

The model was used to evaluate the environmental impact of:

- An upgraded two-stage blow heat recovery system
- Elimination of blow condensates from brownstock showers
- Addition of a fourth washer (after the refiners) to reduce BOD/methanol/HAPs to machines.

Table X shows the projected changes in methanol for the process modifications listed previously. Note that the methanol concentration in the combined condensates used for shower water is reduced by 50%. This results in a significant reduction in methanol carried over to the machines, thus favorably impacting HAP emissions from the machine area.

This impact is shown in terms of methanol loading in Table IX and **Fig. 1** *(13)*. Observe that the modifications are predicted to reduce methanol (and hence HAPs) emissions by 70% from current levels. The modifications are expected to reduce methanol air emissions to 12.5% of the total generated by containing more methanol in condensate streams.

Note in Fig. 1 that NCASI's machine emissions trend line, established from mill surveys, is tracked by Mead data. Methanol/HAP emissions from the machine area is determined by methanol carryover with the pulp stock, level of closure, press conditions, and methanol concentration in key paper machine streams, such as the white water stream. Modern machines with increased white water closure and higher methanol content in white water can potentially release more of the incoming methanol to air emissions.

Option	Stripper flow % total condensate	% Total methanol generated removed
At current conditions (All evaporator condensates)	72	40.0
With modified blow heat recovery:		
Blow condensates	20	48.0
Blow & evaporator condensates	92	73.0
Blow & contaminated condensates	42	58.0
With modified blow heat recovery and pre-evaporator (blow & pre-evaporator condensates.)	44	72.0
Typical stripper at modern kraft mill	...	45.0

VIII. Mill A: Stripping options (alternative 3)

	MODEL RESULTS	
	Current	After modifications
Generated	3.93	3.93
Air emission:		
Digester blow/relief	0.83	0.07
Evap. hotwell	0.26	0.18
Machines dryers	0.70	0.24
Total:	1.79	0.49
Methanol release to air, %	45.5	12.5
To sewer:		
Blow condensates	0	2.27
Evap. condensates	0	0.71
Machine	2.1	0.46
Other	0.04	N/A*

*Not applicable

IX. Mill B: Methanol emission impact summary, lb/o.d. ton semichemical pulp

CONCLUSIONS

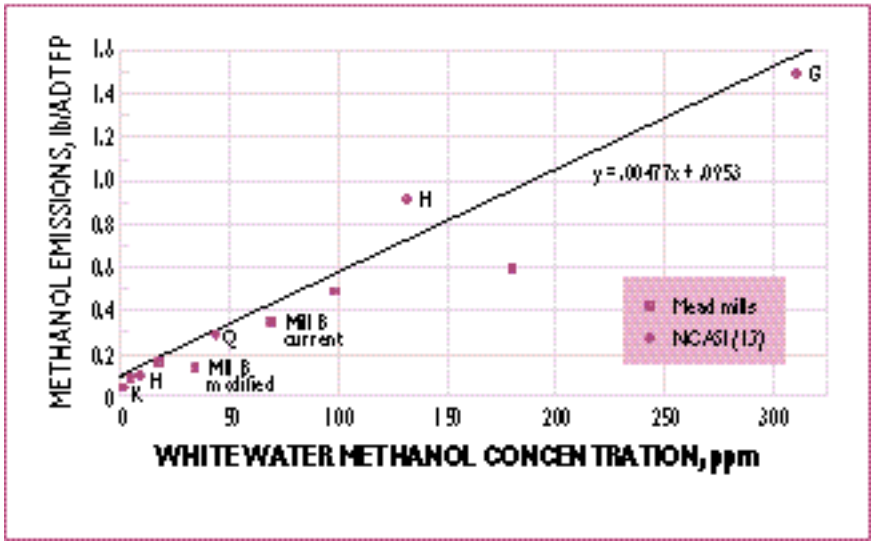
The following conclusions were reached as a result of our work:

- Process simulation with systems such as GEMS is a valid tool to predict methanol concentrations in pulp mill streams for both alkaline and semichemical pulping processes.
- Two case histories presented

Process stream	Mill data	MODEL RESULTS Current	After modifications
Defibrator outlet	280[a] (167–387)[b]	292	310
Weak black liquor	323 (324–347)	304	247
Blow heat condensate	2255	2241	2519
Combined condensate	300 (269–321)	328	164
No. 3 washer mat	276 (258–333)	314	168
Uncondensed blow vapors (Volumetric, wet ppm)	1345 (3062 peak)	1482	N/A[c]

[a]Average ppm (from five daily samples)
[b]ppm range of samples
[c]Not applicable

X. Mill B: Methanol balance—Model validation and impact of process modifications, ppm



1. Methanol emissions from paper machines/pulp dryers

show that, once the mill model is calibrated against operating data, simulation is a useful tool to predict typical methanol content for alternative operating scenarios in liquid and vapor streams.

- Simulation is a useful method to systematize mill HAP data for easier interpretation.
- Methanol content can be used to track HAP levels or other components, such as acetone, methyl ethyl ketone, and acetaldehyde. **TJ**

Venkatesh is manager, process technology at Mead Corporate Engineering, 3131 Newmark Drive, Miamisburg, OH 45342. Lapp is manager, enviromental technology and Parr is senior enviromental consultant at Mead Corporate Human & Enviromental Protection, 3475 Newmark Drive, Miamisburg, OH 45342.

The assistance of the participating Mead mills and laboratory personnel at Mead Corporate H&EP is gratefully acknowledged. Helpful suggestions from H&EP's K. C. Ayers are appreciated.

Received for review Jan. 15, 1996.

Accepted Aug. 15, 1996.

Presented at the TAPPI1996 Environmental Conference.

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