Production of Hydrocarbons from Fast Pyrolysis of Kraft Black Liquor – Integration with the Kraft Mill

Arend Jan Zeeuw[a], Adriaan van Heiningen[b], Jim Wearing[c] , Bart De Waele[a], Xuantian Li[c], Michael Gattrell[c], Chris Chan[c], Clive Brereton[c,d], Brian Blackwell[e], Tony Boyd[c]

[a]Huntsman Polyurethanes, Everslaan 45, B-3078 Everberg, Belgium
[b]University of Maine, Orono, Maine
[c]NORAM Engineering and Constructors, Ltd., 200 Granville St., Suite 1800, Vancouver, BC, Canada
[d]BC Research, Inc. 12920 Mitchell Road, Richmond, BC, Canada
[e]Vancouver BC

ABSTRACT

A proprietary thermochemical process, trade named Emerald Process [1], is being developed for the production of chemical feedstock from Kraft black liquor through fast pyrolysis, catalytic upgrading and separation. The objective of this process is to leverage the harvesting and processing infrastructure of the modern Kraft mill to produce chemical feedstocks in large quantity in addition to cellulose. Integration of the new process with existing and new Kraft mills is key to obtaining maximum economic synergy.

In the proposed process, the fast pyrolysis step takes place in a fluidized bed, where part of the high solids Kraft black liquor stream is pyrolysed. The fine droplets of heavy black liquor coat the solid particles in the circulating bed, while a fluidizable char with favorable particle size distribution and friability is produced in the bed. A small portion of the char particles, separated by cyclones, is oxidized in a solids heater and returned to the pyrolysis reactor to supply the heat required for drying, heating and pyrolysis. The balance of the char, also containing the bulk of the inorganics, is reintroduced to the black liquor for recovery in Tomlinson furnace to maintain the chemical balance and support both chemical reduction and steam production in the boiler. The raw pyrolysis gas is upgraded in a catalytic reactor to improve the yield of aromatics in bio-oil. After separation of the upgraded hydrocarbon product, the non-condensable gases are returned to the recovery boiler.

Following a summary of results with a 10 cm diameter fluidized bed system, this paper will present mass and energy flows for a modern Kraft mill employing the new process and discuss implications for new mill design and methods of char firing in the recovery boiler. An assessment of the economic and environmental merits of this process will be presented.

SUBMITTED COPY

J-FOR - Journal of Science & Technology for Forest Products and Processes

2017, Vol.7, No.4, p. 31-38

INTRODUCTION

In recognition of shifting world interest in renewable, sustainable products and solutions, forest companies around the world are looking at ways to diversify their product range with growth businesses, and serve a greater number of markets from their forest base. Initiatives ranging from bio-fuels to polymers to specialty chemicals have been announced in recent years [2].

At the same time, a number of contextual drivers such as social urgency, tougher legislations and economic competitiveness in a global economy have been incentivizing the Chemical Industry to move away from fossil resources. While long term research is looking at entirely new processes to deliver zero waste manufacturing, for the next 20 years it is likely that most success will come from blending in increasing amounts of bio-based chemicals and fuels with those derived from fossil based feedstock. This will allow the chemical industry to continue using existing or slightly modified assets. Lately, the composition of available fossil based feedstock is shifting towards higher alkane and lower aromatic content, due to the increasing contribution of GTL to the feedstock. To offset this, it would also be desirable that the bio-based supplement is rich in aromatic hydrocarbons, as aromatics are used in the production of a very large number of petrochemicals.

Project Emerald aims to produce chemical feedstock from Kraft black liquor through fast pyrolysis, catalytic upgrading and separation. The process is generically termed K2H, for Kraft to Hydrocarbons in this paper. Fast pyrolysis involves rapidly heating biomass (>500°C s-1) to intermediate temperatures (400–600 °C) followed by rapid cooling (vapor residence times 1–2 s) [3]. The importance of pyrolysis heating rate is well known [4, 5]. One of the advantages of fast pyrolysis is that this technology is economical on a smaller scale so that smaller distributed plants can be built close to the location of the biomass [6, 7]. However, the bio-oils that are produced after the initial fast pyrolysis step are of poor quality. They are thermally unstable, degrade over time, are acidic, have a low heating value, and are not compatible with existing petroleum-derived oils [8]. Bio-oils must be catalytically upgraded if they are to be used as a supplement to conventional feedstock [9-11]. Adding a catalytic upgrading step will convert oxygenated compounds generated from pyrolysis into aromatics [12]. As recent history proved the sensitivity of most upgrading catalysts towards catalyst poisons present in the biomass feed [13], it was decided in the present technology to separate the fast pyrolysis and upgrading sections to allow the creation of an economically viable process based on black liquor, the spent liquor from the Kraft pulping industry.

The unique advantage of the proposed process is to leverage the harvesting and processing infrastructure of the modern Kraft mill to produce chemical feedstock in large quantity in addition to cellulose. The integration of the process into the Kraft recovery cycle has no influence on the inorganic sodium and sulfur balance, and by limiting the fraction of black liquor to be processed to about 1/3, the steam and energy requirements for pulp production in a modern mill can still be met by combustion of the remaining 2/3 in the recovery boiler [14]. In fact, the proposed process can be fully integrated in a modern Kraft mill, and adds no new mill waste streams.

Black liquor has been considered as a feedstock for the production of value-added products for about a century, starting with the Rinman process which produced alcohols, aldehydes, ketones, and hydrocarbons from black liquor by dry pyrolysis [15]. More recent efforts include hydrothermal treatment of black liquor at 350 °C with NaOH addition [16] and atmospheric pyrolysis from 327 to 677 ° [17]. However, in all cases the bio-oils produced still contain large amounts of oxygen, while the integration with the Kraft recovery process is complex. Competing prominent processes to produce biofuels and biochemicals from conventional lignocellulosic feedstock such as wood and wood waste are used for evaluating the economic merits of the proposed K2H process. The aim of the work is to demonstrate the continuous fluidized bed fast pyrolysis of black liquor in a self-sustaining uniform fluidisable char bed and to demonstrate the feasibility of the integration of the K2H process within a modern Kraft mill.

FLUIDISED BED SYSTEM TEST RESULTS

As part of the development, testing was carried out using a bench-scale apparatus, shown in Fig. 1 and Fig. 2. The pyrolysis reactor consisted of a 10 cm ID reactor operating at 540-600°C containing a ~26 cm deep bubbling fluidized bed. Kraft hardwood black liquor with 67% solids content was used in the tests. The reactor off-gases were sent through a cyclone, condenser, filter, and afterburner before being vented. A slipstream could be drawn off for sampling for volatile organic compounds and the slipstream could also be passed through a catalytic reactor to test upgrading catalysts.

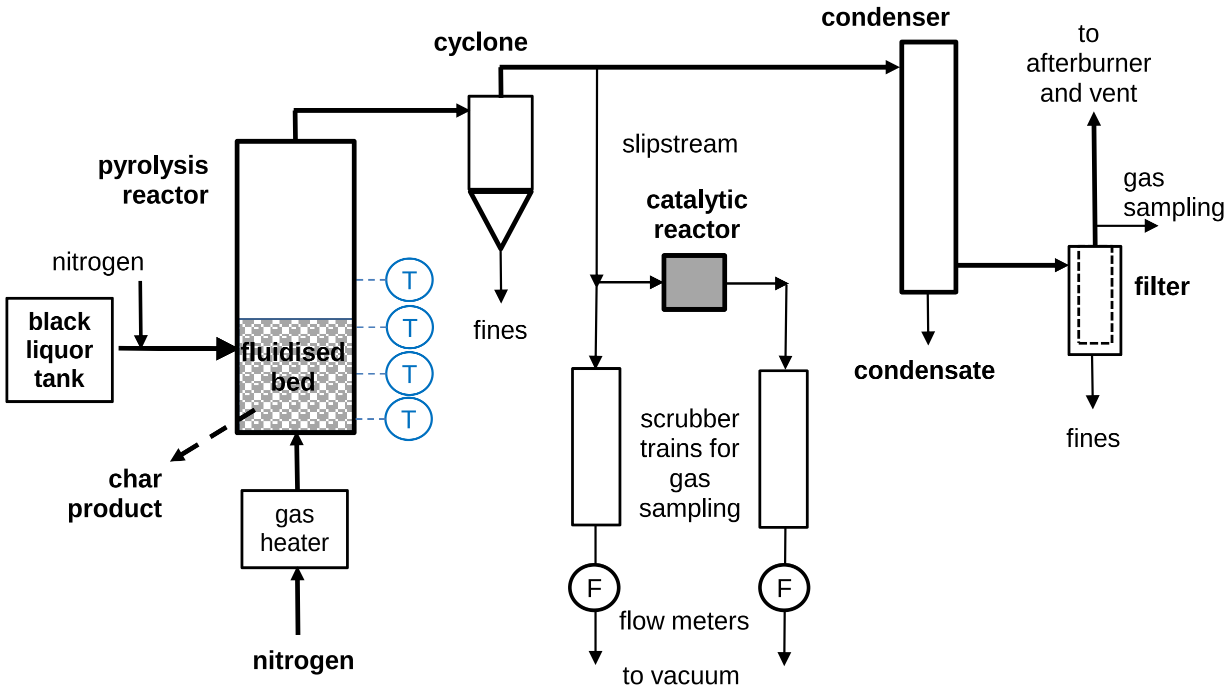

Figure 1: A diagram of the bench-scale pyrolysis test system.

A key focus of the test work was to demonstrate the successful fluidized bed pyrolysis of black liquor. Achieving this required a spray nozzle that could continuously feed and properly atomize the black liquor evenly onto the fluid bed particles. A fine and even spray was required to allow the black liquor to be pyrolysed to generate a fluidisable char with preferable particle size distribution that facilitates integration with the mill.

A second goal was to make sufficient quantities of char to test its properties (chemical composition, physical properties (e.g. density, particle size distribution, porosity, and internal surface area), fluidizability and attrition resistance, etc). Finally, rough mass balances were made for the various inorganic and organic components of the black liquor and products thereof.

After various iterations, a black liquor spray nozzle was developed that was suitable for use at the very small scale of laboratory operation. One important factor was providing a temperature controlled jacket to maintain the black liquor at a suitable temperature for spraying while avoiding flashing where the tip of the nozzle entered the hot pyrolysis reactor. Excessive flashing could leave deposits that could plug the spray nozzle and intermittent flashing could cause uneven flow that could lead to clumping in the fluidized bed or “dribbling” that could lead to fouling of the nozzle tip.

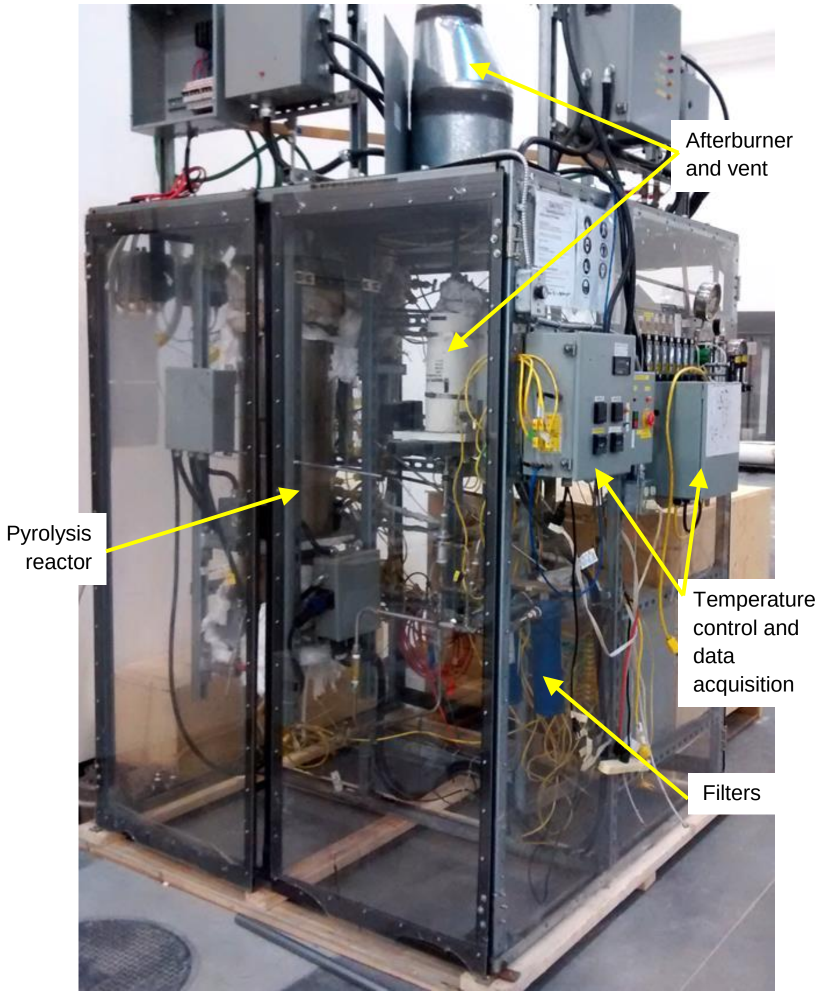

Figure 2: The bench-scale pyrolysis system with surrounding fume cupboard

Fig. 3 is a typical image of the char particles in the bed. The surface of the particles has a "frothy" appearance, likely due the flashing of the water and volatile organic compounds from the black liquor droplets sprayed on the char when they impact and coat the hot char particles.

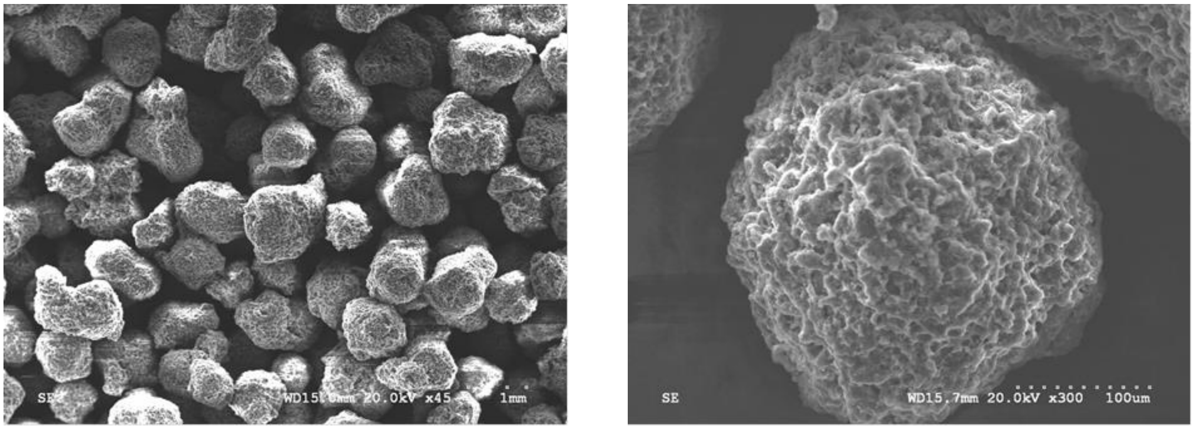

Figure 3: SEM images of fluidized bed black liquor char (Left: 45 x, Right 300 x).

The test system was run in a semi-continuous mode with runs around 1-3 h. The fluidized bed was drained after each run, sieved to remove large particles and re-loaded. The short run times, coupled with loss of material (solids and oils) sticking to piping walls allowed only for approximate mass-balance information.

An elemental analysis of the black liquor dry solids and the pyrolysis char is given in Table 1. The total collected fines typically amounted to ~12 wt% of the sprayed black liquor solids. If one assumes the sodium and potassium are essentially non-volatile at the present low operating temperatures, then the bed char represents ~54 wt% of the black liquor dissolved solids. Combining the bed char and fines gives ~66 wt% of the black liquor solids being non-volatile. This is in agreement with the pyrolysis char yield found by Gairns et al. of 69-67% for mixed hardwood 70% solids Kraft black liquor droplets obtained at 500-600°C [18]. One can also see that the fines have retained more hydrogen and sulfur compared to the bed char, suggesting that they have been less thoroughly de-volatilized, likely because they have spent less time in the pyrolysis bed.

Table 1: Elemental analysis of the black liquor dry solids, the pyrolysis char and fines (from the cyclone and filter).

	Black liquor (wt%)	**Bed Char (wt%)**	**Fines (wt%)**
C	32.8	31.6	34.0
H	3.92	0.54	1.50
O	37.9	33.3	31.3
S	4.05	0.83	2.00
Na	18.1	28.5	21.5
K	3.33	5.21	5.20

It was found that a significant fraction of sulfur is volatilized during the experiments (see Table 1). The approximate distribution of the sulfur compounds in the black liquor was: 51% as sodium sulfide (Na_2S), 24% as sodium thiosulphate ($Na_2S_2O_3$), 10% as sodium sulfate (Na_2SO_4) and 10-20% as organic sulfur compounds. The analysis of the char indicates that most of the sulfur is present as Na_2SO_4 (~90%) and $Na_2S_2O_3$ (~10%). A gas sample was analyzed for sulfur compounds and found hydrogen sulfide (H_2S), methyl mercaptan and dimethyl sulfide. Thus, it appears that most of the starting sodium sulfide and organic sulfur compounds have been volatilized. The sodium sulfide would be converted to volatile hydrogen sulfide by the equilibrium reaction:

$$Na_2S(s) + H_2O(g) + CO_2(g) \Leftrightarrow H_2S(g) + Na_2CO_3(s) \qquad (1)$$

The present temperatures are too low for significant reduction of sodium sulfate to sodium sulfide. The organic sulfur compounds decompose during pyrolysis to hydrogen sulfide, methyl mercaptan and dimethyl sulfide as has been shown by Li and Van Heiningen [19]. The results show that under the humid and reducing pyrolysis conditions and with the long char hold time of this work, a large portion of the starting sulfur in the black liquor (~60-80%) ends up as volatile H_2S and sulfur-organic compounds.

Overall, the bench-scale testing was able to successfully demonstrate the semi-continuous bubbling fluidized bed pyrolysis of the black liquor, generating a self-sustaining uniform fluidisable char bed. In addition, insights were gained into the pyrolysis reactions and the distribution of products that might be expected from a larger scale system.

INTEGRATION OF THE K2H PROCESS IN A KRAFT PULP MILL

Base chemical production requires economy of scale. The present decade has seen phenomenal increases in the size of Kraft pulp mill operations, particularly those based on hybrid hardwood plantations [20]. Thus, one important scenario is the integration of the process with such a Kraft mill. Presented below are estimates for a hypothetical 4500 ADt/d single-line Eucalyptus Kraft pulp mill. The pulp mill operates with 52% unbleached yield, 1.4 t solids/ADt pulp with 14.6 MJ/kg calorific value. Material and energy balances were performed using an in house developed Excel model, linked to an Aspen simulation of the K2H process. Key findings and conclusions with respect to the host pulp mill are summarized below.

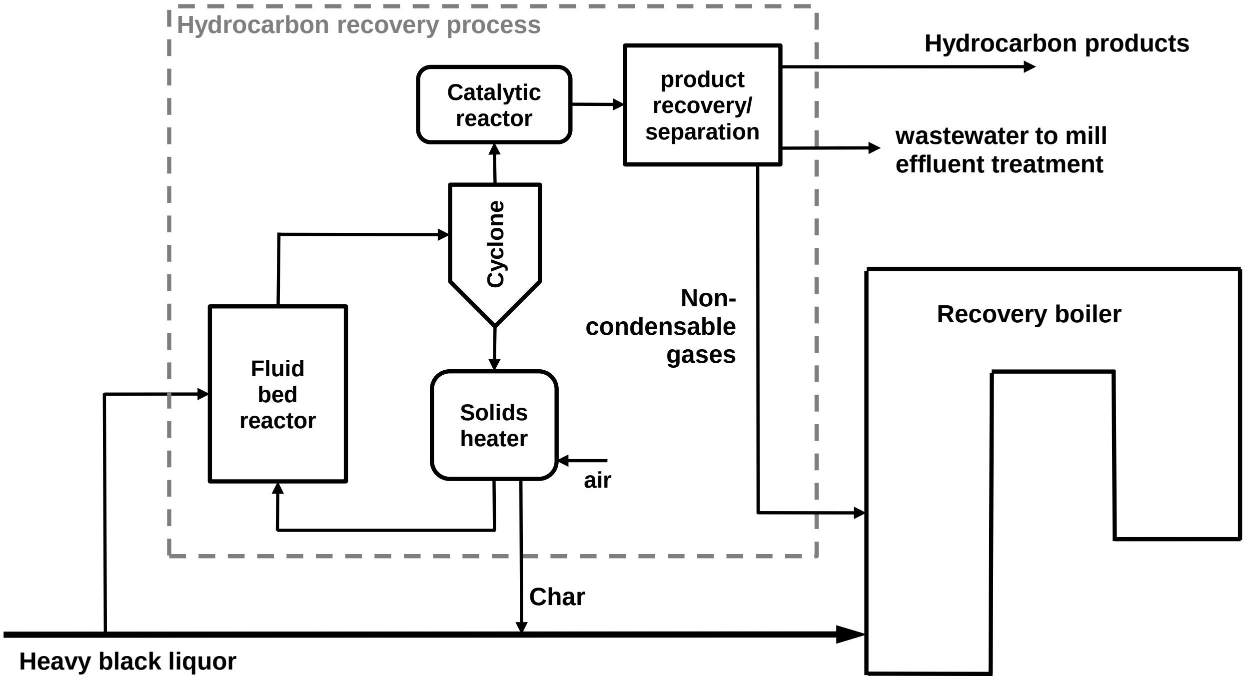

Figure 4 Flowsheet of the integration of the K2H Process in a Kraft pulp mill recovery boiler

In the integrated flowsheet (see Fig. 4) one third of the heavy black liquor is diverted to the fluid bed reactor. The K2H process produces four process flows: the Hydrocarbon Products, cooled char, residual non-condensable synthesis gas and wastewater. The Char is mixed with the remaining black liquor with no comminution and fired using modified nozzles into the recovery boiler. The Residual Synthesis Gas is fired at the load burner area in the recovery boiler through appropriately sized CNCG nozzles.

Material and energy flows are presented in Table 2. Sodium losses in the K2H process are negligible and thus the sodium cycle of the integrated mill remains the same as conventional operation.

Table 2: Material and Energy Flows in the Integrated Kraft pulp mill K2H Process

Component	Heavy Black Liquor	Hydrocarbon Product	Char	Residual Synthesis Gas	Fired Mixed Liquor
Organic, t/d	3840	300	340		2870
Inorganic, t/d	2460	-	795		2470
Calorific Value, GJ/d	92100	12400	6800	8300	68200

The sulfur balance in K2H cannot yet be established. Thermodynamics favor sulfur volatilization at the lower temperatures and the reducing atmosphere proposed for the Fast Pyrolysis Reactor. The experimental results bore this out. However, as the industrial implementation will employ fast pyrolysis with residence times on the order of 2 s; kinetic limitations may reduce the sulfur emission significantly. In the Solids Heater, the residence time is long, but the temperature is higher and since oxygen is admitted to increase the temperature, the environment is no longer strictly reducing. For these reasons, a more accurate sulfur balance will be established at a larger scale, where an equipment setup can be used that is more representative for the commercial process. In the Recovery Boiler, sulfur compounds evolved in the K2H process will be combusted to SO_2 and combine with excess carbonate in the upper boiler regions to form sodium sulfate. In this form it will ultimately be returned to the fired black liquor. In recently built Kraft recovery boilers, carbonate levels are high in the ash, typically 20% as CO_3. Such a boiler would see a reduction from 20% to 3% carbonate in ash if 50% of the sulfur were volatilized in the K2H Process. This is within a practical operating range and would not require further design change. If the volatilization fraction is higher than the assumed 50%, or if a higher percentage of black liquor were routed to hydrocarbon recovery, then a sulfur removal strategy will be needed. The calorific load on the recovery boiler is reduced from 92100 to 76500 GJ/d, or 17%. The calorific value of the hydrocarbon byproduct constitutes 13% of calorific load decrease, the balance being losses to heat in the K2H process. Water load to the Recovery Boiler is reduced by 33% due to diversion of liquor to Hydrocarbon recovery. This is counterbalanced by thermal requirement for additional sulfate reduction in the recovery boiler caused by sulfation of the carbonate in the upper furnace. These changes are expected to be within the range of present design and do not require special adaptation.

The main impact on mill utilities is the additional steam required to compensate for reduced Recovery Boiler thermal input. Modern Kraft pulp mills typically have a thermal excess of similar magnitude, meaning that this could be in balance in a typical site. As a result of excess energy, bark is often left in the plantations rather than bringing it to the mill site for steam and power generation. The incorporation of hydrocarbon co-production by the mill provides further incentive for complete utilization of bark and other residual biomass. At the design phase, reduced steam generation capacity at the Recovery Boiler is compensated by additional capacity in the Hog Fuel Boiler. The impact on pulp mill utilities is shown in Table 3.

Utility requirements of the K2H Process are rather small. Effluent may be treated in the mill's activated sludge facility where it would represent less than 1% of the flow. There are no emissions to air. All gaseous streams are incorporated in the synthesis gas stream returned to the Recovery Boiler.

Table 3. Summary of major impacts in Pulp Mill Utilities

	Fuel Demand (GJ/d)	Steam Production (GJ/d)	Cooling Water Duty (GJ/d)	Effluent (m^3/d)
K2H Process	+1,000	+1600	+1,200	+600
Hog Fuel Boiler		+16000		

FIRING BLACK LIQUOR - CHAR MIXTURES

To ensure a full integration of the K2H process in the Kraft mill, the char coming from the solids heater is sent to the recovery furnace by mixing it into the un-diverted black liquor (Fig 4). The estimated composition of this black liquor-char mixture is presented in Table 4.

Table 4: The estimated composition of the Heavy black liquor vs. the mixture of char and black liquor as would be fired in the K2H process

	Heavy black liquor flow (t/h)	Fired Liquor Flow (t/h)
Char		47
Black liquor solids	263	175
Water	66	44
Total	328	266

The black liquor-char mixture that would be sprayed into the recovery furnace would have different properties than normal black liquor. Because of the presence of the char, the mixture will have a lower water content, a lower organic content and a higher inorganic content (Table 2). The organic component will also have fewer volatiles. The lower net calorific value (Table 2) may suggest that it would be desirable to deliver more of the spray to the char bed to maintain the required reducing environment. However, less energy would be used to vaporize water and volatile organic compounds. Thus some work will be required to determine the optimal drop size range for spraying these mixtures into a recovery furnace.

Another important factor in successfully spraying black liquor into a recovery furnace is the drop swelling characteristics. To test this, char samples from the bench-scale tests were mixed with black liquor and sent to Abo Akademi University for single droplet combustion tests. The results did not show any measurable significant change in the combustion characteristics as a result of char addition.

The addition of char to black liquor resulted in an increase in viscosity. Tests were conducted using 57-67 wt% dissolved solids black liquor and focused on the impacts that might occur at high black liquor diversions (50-60%). At high char loadings, a significant viscosity increase was found, which appeared to be due to two factors. The first factor is that simply adding inert particles to a fluid will cause an increase in the viscosity related to the volume fraction of particles added [21, 22]. The second factor is that some part of the char appears to dissolve, raising the dissolved solids content of the black liquor and so also increasing the viscosity. A simple model was developed to estimate the effects of these two factors and the results are plotted in Fig. 5 along with some measured data. One can see that with increased black liquor diversion through the K2H process, modifications to spray a high viscosity mixture would be needed. The partial dissolution of the char was also observed to cause a decrease in the Residual Effective Alkali (REA), indicating some buffer capacity in the char, possibly due to bicarbonate. However, adding caustic to re-adjust the REA of the mixture back to the original black liquor value did not significantly lower the viscosity, indicating that the REA was a less important influence on viscosity, at least for the black liquor tested in this work.

For a high-solids black liquor and 33% black liquor diversion to pyrolysis, the largest factor influencing the viscosity will be the slurry effect. In Fig. 5, a Maron and Pierce power law function [22] is used to plot the impact of the char slurry on the black liquor viscosity. As can be seen in the scatter of the measured data, other factors also play a role. These other factors could include chemical effects related to the partial dissolution of the char particles and physical effects such as non-uniformities in the char particle size distribution, char particle shape, and char particle agglomeration. However, while the exact viscosity increase would depend on the specific black liquor used and the characteristics of the generated char, Fig. 5 gives a rough idea of the potential viscosity increase for the mixture to be sprayed into the recovery furnace.

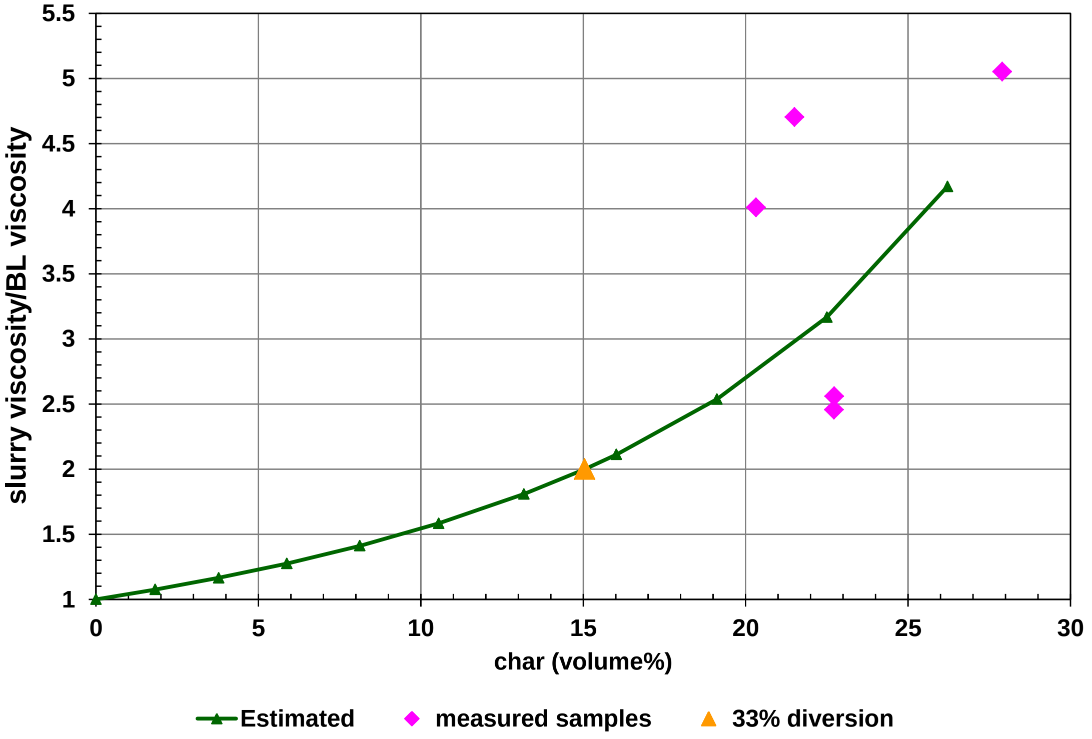

Figure 5 Predicted viscosity increase for black liquor-char mixtures. A 33% diversion of black liquor to pyrolysis is expected to result in a black liquor-char slurry containing ~15 volume% char.

These different properties for the black liquor-char mixture will require changes to the black liquor spraying and in particular the spray drop size distribution to ensure optimal furnace operation. Some variables that could be used to adjust the mixture spraying include: temperature, spray nozzle diameter, mixture dilution and/or mixture chemical modification.

Temperature in the non-flashing region only has a weak effect on drop size and so can only be used for fine tuning. However, temperature in the flashing region could be used to control the drop size. It is known that the nozzle diameter can also be used to control the drop size [23]. However, using a smaller nozzle size to offset a high black liquor viscosity will result in a higher nozzle pressure drop and so may require upgrading the black liquor pumping system for higher pressure operation. Using a more dilute black liquor to mix with the pyrolysis char can lower the mixture viscosity. Finally, while the effect of adding caustic to the black liquor-char mixture was minimal in these tests, adding caustic or other chemical modifications might have some influence on viscosity for other black liquors [24].

ECONOMIC AND ENVIRONMENTAL MERITS

The economic and environmental benefits of the process arise from the synergy of deriving both traditional products and hydrocarbon feedstock from the same forest operation. Duplicate harvesting and land use are avoided. Sustainable forest harvesting, developed over decades of advancements by forest companies forms the basis of land use practices. In the K2H process the transportation of the biomass, wood chipping (at a lower energy demand than grinding) and energy cost for water removal to concentrate black liquor at multiple effect efficiency (at about 5 kg water/kg steam the energy requirement on a dry mass basis is less than biomass drying) are all already accounted for by the pulp production. Considering that there is no new mill waste stream produced, it may be stated that the environmental impact of the K2H process will be very limited. Full implementation will reduce the GHG emission of the host pulp mill.

A more complete use of the harvested wood arises, especially in cases where it is impractical to deliver excess energy to an electric grid. Per ton of wood, a pulp mill produces about 500 kg of pulp, the K2H process would add minimally 45 kg of aromatic rich bio-oil to this. The sales price of this bio-oil at which the required investment return is generated is about 1.85 USD/gallon.

A final interesting observation is that the K2H process upgrades the lignin fraction of biomass, which is the most condensed and hardest to valorize fraction of biomass. All the cellulose is converted to pulp. Also the energy demand of the K2H process compares very well with processes which convert the entire biomass into hydrocarbons because the biomass transportation, wood processing, and water removal are all already accounted for by the pulp production process.

CONCLUSION

A flowsheet for the integration of the K2H process in a Kraft paper mill is proposed. It is shown how the proposed K2H process is expected to mainly impact the mill's sulfur balance, the calorific load to the recovery boiler and the mill's utilities, and it is explained why these changes are expected to be manageable.

Semi-continuous fast pyrolysis of black liquor in a fluidized bed was demonstrated on a 10 cm diameter fluidized bed system. Sufficient quantities of char were produced to test its composition, physical properties and to research its mixing behavior with black liquor.

To ensure a full integration of K2H in Kraft paper mills, the char needs to be sent back to the recovery boiler to close the mill's inorganics cycle. It is proposed to mix the char with the un-diverted black liquor. It is shown that this can be done without a significant change of drop combustion characteristics, and that it is possible to handle the expected viscosity changes.

The unique advantage of the proposed process is to leverage the harvesting and processing infrastructure of the modern Kraft mill to produce chemical feedstock in large quantity in addition to cellulose. The process is fully integrated and produces no new mill waste streams, while reducing GHG emissions. The produced bio-oil is rich in aromatics and can be produced at a very competitive price.

REFERENCES

1. Pending patent application Pub. Nr. WO2016/046161
2. 2016 Annual reports, Fibria, Stora Enso, Domtar, UPM, and related press releases
3. Bridgwater AV (2003) Chem Eng J 91:87
4. Goyal HB, Seal D, Saxena RC (2007) Renew Sustain Energy Rev 12:504
5. Demirbas A (2007) Energy Sour A Recov Utilizat Environ Effect 29:753
6. Bridgwater AV (1992) Energy Fuel 6:113
7. Wright M, Brown RC (2007) Biofuels Bioprod Bioref 1:191
8. Mohan D, Pittman CU Jr, Steele PH (2006) Energy Fuel 20:848
9. Adam J, Antonakou E, Lappas A, Stoecker M, Nilsen MH, Bouzga A, Hustad JE, Oye G (2006) Microporous MesoporousMater 96:93
10. Horne PA, Williams PT (1996) Fuel 75:1043
11. Nokkosmaki MI, Kuoppala ET, Leppamaki EA, Krause AOI (2000) J Anal Appl Pyrol 55:119
12. Carlson TR, Vispute TP, Huber GW (2008) ChemSusChem 1:397
13. http://www.biofuelsdigest.com/bdigest/2016/05/17/kior-the-inside-true-story-of-a-company-gone-wrong/
14. Gellerstedt, Tomani, P., Axegard, P., Backlund, B. (2013) Lignin Recovery and Lignin-Based Products, in: L. Christopher (Ed.), Integr. For. Biorefineries Challenges Oppor., The Royal Society of Chemsitry, Cambridge, pp. 180–210.
15. Rinman, E.L., 1924, ”Rinman process for cellulose manufacture”, Paper 35(1924), 224–226
16. P. McKeough, R. Alén, A. Oasmaa, A. Johansson, Thermochemical Conversion of Black Liquor Organics into an Oil Product. I. Formation of the Major Product Fractions, Holzforschung. 44 (1990) 445–448
17. Gairns, S.A., Fast pyrolysis of kraft black liquor, Master's Thesis, Department of Chemical Engineering, McGill University, Montreal Canada September 1993
18. Li, J., van Heiningen, A.R.P., 1991. Sulfur emission during slow pyrolysis of kraft black liquor. Tappi J. 74 (3), 237-239.
19. V. Sricharoenchaikul, "Sulfur Species Transformations and Sulfate Reduction During Pyrolysis of Kraft Black Liquor", Master of Science Thesis, Oregon State University, (1995)
20. Media Releases by Fibria, Suzano and Sinar Mas, 2015-present
21. H.J.H. Brouwers, "Viscosity of a concentrated suspension of rigid monosized particles", Phys. Rev. E, 81 (2010) 51402.
22. S. Mueller, E.W. Llewellin and H.M. Mader, "The rheology of suspensions of solid particles", Proc. R. Soc. A, 466 (2010) 1201–1228.
23. H.J. Empie, S.J. Lien,W.R. Yang and T.N. Adams, "Spraying characteristics of commercial black liquor nozzles", Presentation Int. Chem. Recovery Conf., Inst. Paper Sci. Tech., June (1992).
24. A.L. Fricke and A.A. Zaman, "A comprehensive program to develop correlations for the physical properties of kraft black liquor", DOE CE-40740-10 (1998).