Process Systems Considerations in Forest Biorefineries with Thermochemical Processing of Wood Wastes

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Introduction

Integration of plants that produce syngas-derived fuels and chemicals with chemical pulp mills, the integrated Forest BioRefinery Concept, has the potential of reducing the overall cost of producing both pulp/paper and biomass-derived chemicals/fuel products. The savings are achieved by (a) reducing the capital cost for gasification of black liquor and wood wastes in an integrated biorefinery as compared with separate pulp mills and fuel/chemical plants, and by (b) increasing the yield of power and chemicals or fuels by integration of mass and heat exchange between the two parts of the integrated complex.

Another potential advantage, when black liquor is gasified, is increased pulp yield. During gasification, at least part of the sulfur in black liquor is converted to H_2S instead of Na_2S. The separation of sulfur from sodium before the pulping chemicals are regenerated makes it possible to produce polysulfide or other alternative pulping liquors for higher yield pulping.

Several other factors must be considered in the design of integrated forest biorefineries. One is the need for a carefully designed energy exchange network to minimize entropy generation. Another is the need to minimize the production of $NaHCO_3$ and the accompanying increase in lime demand for causticizing when regenerating pulping liquors. A third factor is the need and availability of technology for removing contaminants – especially tar, alkali metals, and halides – from the synthesis gas produced.

In this paper, we explore in more detail the opportunities and process integration requirements for highly efficient Forest BioRefineries that are based on production of both wood pulp fiber, and chemicals or fuels via thermochemical conversion of forest residuals and process wastes to synthesis gas.

Pulping Options with Gasification

Gasification of black liquor (BLG) and wood waste is currently being considered as a promising alternative to conventional combustion of these waste fuels. The main advantage for pulping with BLG compared to combustion and conventional recovery of chemicals from black liquor is the possibility of separating sulfur and sodium in the chemical recovery process, thereby facilitating modified or new pulping processes, which can increase the yield of raw papermaking fiber (pulp) from wood. Earlier studies have shown that during gasification of kraft black liquor much or all of the sulfur in the black liquor ends up in the gas phase while the sodium ends up in the solid or molten smelt phase. This provides the opportunity to create sulfur-lean/sulfur-rich cooking liquors that will enable the use of alternative pulping processes that provide certain advantages over conventional kraft.

Some of the pulping options considered here are a variation of the kraft process, polysulfide with anthraquinone (PSAQ), and sulfite based pulping processes such as alkaline sulfite with anthraquinone (ASAQ) or mini-sulfide sulfite with anthraquinone (MSSAQ). A summary of these pulping options compared to kraft is shown in Table I. Typical results and cooking liquor compositions for unbleached softwood (linerboard) grade pulps[1] are shown in Table II and for bleached softwood grade pulps are shown in Table III.

Polysulfide Pulping with Anthraquinone (PSAQ)

A modification of the kraft process that would be enabled with a sodium/sulfur split in gasification is polysulfide pulping. A portion of the sulfide (about 60%) is oxidized to elemental sulfur in the cooking liquor, forming a polymeric compound represented as $Na_2S{\cdot}S_x$. The presence of polysulfide in the first stages of the cook provides some protection against alkali degradation of the carbohydrates thus increasing pulp yield. The yield increase is a direct function of the amount of polysulfide that can be applied in the cook. In conventional kraft recovery systems, polysulfide is formed by oxidizing the white liquor in the presence of a catalyst. The amount of polysulfide formed is limited by the oxidation efficiency and the need to avoid over oxidation of the sulfide to sulfate or thiosulfate. Separation of sulfur in gasification provides the opportunity to tailor the amount of polysulfide used in pulping. Some or all of the H_2S from gasification is directed to Claus reactors where elemental sulfur is formed then redissolved in the cooking liquor to form the polysulfide. Anthraquinione (AQ) added to the cooking liquor has a synergistic effect with the polysulfide to further increase yield. AQ also serves as a catalyst to increase the delignification rate. Cooking with PSAQ liquors increases the pulp yield by an absolute amount of 2-4% compared to conventional kraft[2].

Alkaline Sulfite Pulping (ASAQ and MSSAQ)

There are several advantages to sulfite processes that make them candidates for replacement of kraft pulping. The adoption of these has been limited however by the lack of efficient recovery systems. BLG provides the opportunity to produce sulfite cooking liquors.

ASAQ pulping has been reported to give substantially higher yields (by 2-4% at kappa number 30 and by 7% at kappa number 85) than the kraft process. Pulping processes based on ASAQ also have much lower potential for producing foul odors than the kraft process. ASAQ pulps are similar in strength but brighter than corresponding kraft pulps[3]. The ASAQ process is capable of cooking to a wide range of kappa numbers, both unbleached and bleached grades. Pulp bleachability is better than kraft pulps. The rate of delignification is slower than for kraft, however, and higher cooking temperatures and longer times are required.

Preparation of ASAQ pulping liquors would require nearly 100% separation of the sulfur as H_2S which would then be converted to SO_2 in a sulfur burner. The SO_2 would be absorbed in the cooking liquor to form sodium sulfite. The ASAQ process would also require a causticizing step to convert Na_2CO_3 to NaOH.

An alternative to ASAQ pulping was developed by STFI and was termed the minisulfide-sulfite-anthraquinone (MSSAQ) process[4]. For MSSAQ pulping, the prefix “mini” refers to a low charge of sulfide in an alkaline sulfite pulping liquor, and this is the characteristic of the process. The optimum ratio of sulfide to (sulfide+sulfite) was found to be in the range of 0.05-0.15 and that higher ratios resulted in less delignification[5]. Application of the MSSAQ process was proposed to consist of adding 10-15% of green liquor to the sodium-based sulfite liquor. In addition to sulfide, the liquor would also contain a certain amount of carbonate.

No free alkali is added as NaOH in MSSAQ liquors but it is proposed that some is formed from sulfide and carbonate according to the reactions:

$$S^{-2} + H_2O \Rightarrow HS^{-} + OH^{-} \qquad [1]$$

$$CO_3^{-2} + H_2O \Leftrightarrow HCO_3^{-} + OH^{-} \qquad [2]$$

Compared with other alkaline sulfite processes, the MSSAQ process requires less pulping chemicals and a shorter pulping time as a result of faster delignification. Compared to the kraft process, delignification is slower. The yield advantage for MSSAQ compared to kraft is as much as 10% at high kappa numbers but this advantage becomes less with decreasing kappa number. The MSSAQ process has its best advantages in the kappa number range of 50-100 for softwoods. For high-kappa unbleached grades, the MSSAQ pulp was brighter (40% ISO) than a kraft pulp (18% ISO). The MSSAQ pulp was also easier to beat, requiring 25% less energy to reach a given tensile strength[6].

Bleachable-grade pulps are not possible with single-stage MSSAQ pulping but additional delignification could be accomplished with a second pulping stage or an oxygen stage.

The MSSAQ process would require 85-90% of the sulfur as H_2S to form SO_2 with the remainder as Na_2S. Since no additional alkali is used, a causticizing step would not be needed, resulting in significant savings in energy costs.

For high-yield unbleached grades such as linerboard, MSSAQ pulping is an attractive option because of the significant yield increase, thereby reducing wood costs or increasing production. Significant energy savings are also realized with elimination of the causticizing cycle and lime kiln.

For bleachable-grade pulps, either PSAQ or ASAQ provide similar yield advantages compared to kraft. ASAQ has the advantages of lower odor, higher brightness, better bleachability, and somewhat higher strength compared to PSAQ.

Table I. Summary of Sulfur-Based Pulping Options

	Kraft	**PSAQ**	**MSSAQ**	**ASAQ**
Applicability	Readily pulps SW and HW from unbleached to bleached grades	Variant of kraft pulping. Same applicability.	Limited to kappa nos. of 50 or higher for unbleached grades	Pulps SW and HW for unbleached and bleached grades.
Rate	Fastest delignification rate	Rate similar to or slightly less than kraft due to lower sulfidity.	Rate slower than kraft but somewhat faster than ASAQ. Differences are small at high kappa nos.	Requires higher temperature and longer time than kraft Somewhat slower than MSSAQ.
Yield	Lowest yield. About 56% at kappa 100 and 45% at kappa 30.	Yield 2-4% higher than kraft.	8-10% higher than kraft at high kappa nos. Yield advantage decreases at lower kappa nos.	3 to 7% higher than kraft depending on kappa no.
Brightness	Low brightness	Same as kraft.	10-20 points higher than kraft	10-20 points higher than kraft
Strength		Somewhat lower tear than kraft, other properties similar.	Refining 25-30% less than kraft. Similar or slightly higher strength than kraft except for lower tear.	Less refining than kraft. Similar or slightly higher strength than kraft for lower tear.
S Split with Gasification	100% as Na_2S required.	60% as H_2S to Claus reactors to make elemental sulfur. 40% as Na_2S.	10-15% as Na_2S and 85-90% as H_2S to make Na_2SO_3.	100% as H_2S to make Na_2SO_3.
Causticizing With Gasification	Increase in causticizing deamnd	Increase in causticizing demand	No causticizing required.	Increase in causticizing demand

Table II Typical Results and and Chemical Requirements for Kraft and Sulfite Pulping Options for Unbleached (Linerboard) Grade Pulp

Process	Kappa	% Total Yield	% Total Chemical	% NaOH	% Na_2S	% Na_2SO_3	% Na_2CO_3	%AQ
Kraft	100	56	18.6	11.2	4.8	0	2.6	0
PSAQ	100	60	18.3	12.3	1.9/1.5*	0	2.6	0.1
ASAQ	100	61	20.0	2.0	0	16	2.0	0.1
MSSAQ	100	67	22.0	0	2.2	17.6	2.2	0.1

Chemical as %Na_2O by weight on o.d. wood
*% polysulfide on od wood

Table III. Typical Results and and Chemical Requirements for Kraft and Sulfite Pulping Options for Bleached Grade Pulp

Process	Kappa	% Total Yield	% Total Chemical	% NaOH	%Na_2S	% Na_2SO_3	% Na_2CO_3	%AQ
Kraft	30	45	22.2	13.3	5.7	0	3.2	0
PSAQ	30	48	23.2	15.3	3.0/1.7*	0	3.2	0.1
ASAQ	30	49	34.0	9.6	0	14.4	10	0.1

Chemical as % Na_2O by weight on o.d. wood
*% polysulfide on od wood

Recovery and Regeneration of Pulping Chemicals

To evaluate options for producing pulping liquors for alternative pulping processes based on sulfur-sodium separation during gasification of black liquor, it is necessary to understand the extent of separation achievable and how that depends on gasification conditions. The key process variables of interest are pressure, temperature, oxygen-to-fuel ratio, the dry solid content of black liquor, and the liquor sulfur to sodium ratio.

Thermodynamic equilibrium calculations were used to evaluate the impact of these variables on the distribution of sulfur, alkali metals, and chloride between the gaseous and condensed phase products of gasification of black liquor. FACTSAGE™, a commercially available software package was used for this purpose. It is considered one of the best available for thermodynamic calculations where both gas mixtures and condensed phase mixtures of inorganic salts are present[7].

The amount of gas phase sulfur increases as temperature is decreased and pressure is increased. Figure 1 shows the fraction of sulfur in the gas phase at equilibrium for air-blown atmospheric gasification at 950^oC, and oxygen-blown pressurized gasification at 950^oC and 30 bar. The results are depicted in Figure 1 as a function of air factor, the ratio of oxygen input divided by the stoichiometric oxygen demand for complete combustion. At a typical air factor of 0.45, approximately 20% of the sulfur is in the gas phase at atmospheric high-temperature gasification, and approximately 70% at pressurized gasification under the conditions studied. 99% of the gas phase sulfur is H_2S at equilibrium, with COS constituting most of the remainder. Increasing the air factor increases the fraction of sulfur in the gas phase. The fraction of gas phase sulfur decreases as liquor solids content increases.

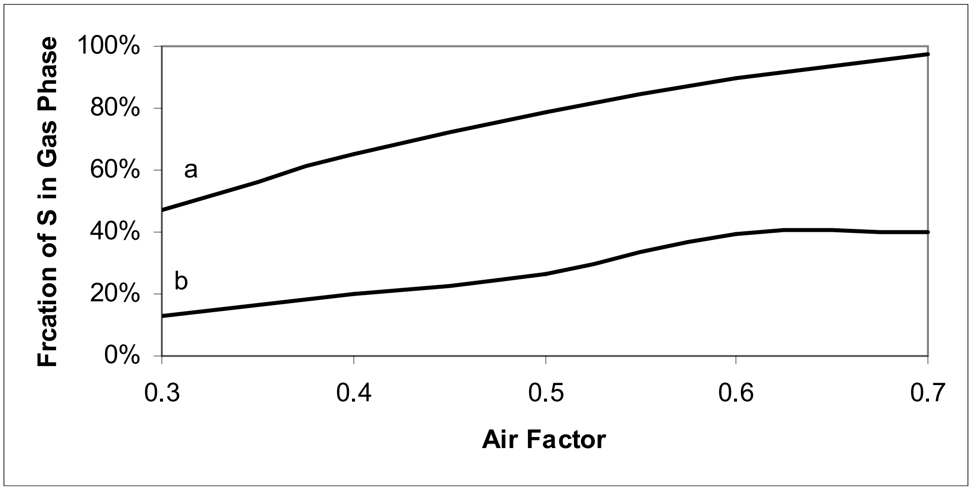

Figure 1.Fraction of sulfur in gas phase for a) pressurized oxygen-blown gasification at 950°C and 30 bar, and b) atmospheric air-blown gasification at 950°C. Liquor solids content 80% and S content 4.3%.

During low-temperature gasification close to 100% of sulfur is released into the gas phase and thus low-temperature gasification produces higher fractions of gas-phase sulfur than high-temperature gasification.

The gas phase sulfur which is mainly in the form of H_2S, needs to be recovered from the product gas, converted into suitable form for liquor recovery (elemental sulfur for PSAQ, and SO_2 for sulfite pulping processes) and recombined with the pulping liquor stream to produce the required pulping chemicals.

Several processes exist for the recovery of H_2S from the gasifier product gas. Absorption into liquid phase sorbents in processes such as Rectisol® or Selexol® are proven commercial technologies that are widely used in the petroleum industry and also for fuel gas from coal gasification. However, these processes are capital intensive and require cooling the product gas to very low temperatures (in the case of Rectisol® to as low as -40°C), which is associated with substantial thermal efficiency losses. Absorption into solid sorbents such as zinc oxide or titanates and subsequent regeneration of H_2S by e.g. steam treatment does not require the same amount of cooling and is more economically attractive. However, the processes are not currently at the same stage of commercial maturity as liquid absorption technologies. All the sulfur recovery technologies produce concentrated H_2S streams that can be utilized to regenerate the pulping chemicals.

For kraft pulping, any gas phase sulfur in the product gas needs to be converted to Na_2S. This could be done by absorption of H_2S into green liquor which is the method of sulfur capture at the existing atmospheric high-temperature gasifier. The absorption into green liquor, however, results in co-absorption of CO_2 which increases the causticizing demand and thus lime demand. The increase in lime demand is discussed more in detail below.

For polysulfide pulping, approximately 60% of the sulfur is required in the form of elemental sulfur and the rest as Na_2S. H_2S can be converted efficiently into elemental sulfur by a Claus process, and polysulfide can be generated by adding the elemental sulfur into white liquor. The amount of sulfur needed as H_2S for polysulfide pulping matches well with the amount of sulfur available in the gas phase from pressurized high-temperature gasification, and all H_2S generated could be converted to elemental sulfur. However, a higher proportion of sulfur is converted to gas phase during low-temperature gasification. Any extra gas-phase sulfur that is not required as elemental sulfur would need to be captured into the liquor as Na_2S by e.g. green liquor absorption which increases the lime demand.

For MSSAQ and ASAQ pulping, the H_2S-rich gas from the sulfur-capture unit can be burnt to produce SO_2, and sodium sulfite can be formed by sorption of SO_2 into the liquor. The percentages of sulfur required as H_2S for MSSAQ and ASAQ are 85-90% and 100%, respectively. This high fraction of gas-phase sulfur can be obtained by low-temperature gasification but not by high-temperature gasification. The fraction of sulfur in the gas phase from low-temperature approaches 100%, and is thus somewhat higher than the requirement for gas-phase sulfur for MSSAQ pulping. Any H_2S exceeding the requirement for sulfite formation can be absorbed into the liquor as Na_2S. As discussed previously, no NaOH is necessary for MSSAQ pulping, which totally eliminates the causticizing step. Hence, the capture of H_2S is not associated with increased lime requirement for MSSAQ pulping. High-temperature gasification even at pressurized conditions may not produce sufficient fractions of gas phase sulfur for MSSAQ and ASAQ pulping. Hence the integration of these pulping technologies with high-temperature gasification would require additional steps to produce H_2S with associated costs.

Increase in Lime Demand

Some of the liquor recovery processes are associated with extra causticizing need and thus increased lime demand. Lime kilns are major consumers of fossil fuel in pulp mills, and they may also be capacity bottle necks. There are two sources for the increased lime demand. One source is the co-absorption of CO_2 during absorption of H_2S into green liquor. The stream from which H_2S is absorbed always contains CO_2, and some CO_2 becomes co-absorbed and sodium bicarbonate is formed.

$$CO_2 + Na_2CO_3 + H_2O \Rightarrow 2\ NaHCO_3 \qquad [3]$$

During causticizing, sodium bicarbonate is converted to caustic.

$$2NaHCO_3 + 2Ca(OH)_2 \Rightarrow 2\ NaOH + 2\ CaCO_3 + 2H_2O \qquad [4]$$

The net impact of CO_2 co-absorption is that one extra mole of $Ca(OH)_2$ is required for each mole of CO_2 absorbed.

The amount of CO_2 co-absorbed during green liquor absorption depends on the selectivity of H_2S absorption over CO_2 absorption, the ratio of H_2S to CO_2 in the gas, and the fraction of H_2S absorption desired. The product gas from the gasifier contains a high ratio of CO_2 to H_2S, typically of the order of 10 moles of CO_2 per mole of H_2S. If H_2S is absorbed directly from the gasifier product gas, a large amount of CO_2 becomes co-absorbed even if the selectivity of H_2S to CO_2 is high. If H_2S is absorbed from a concentrated H_2S stream such as after a sulfur recovery unit, the CO_2 to H_2S ratio is more favorable (typically one mole of CO_2 per mole of H_2S). Consequently, considerably less CO_2 becomes co-absorbed, which leads to lower increase in lime demand than if H_2S is absorbed directly from the product gas.

A second source for increased lime demand with gasification stems is directly the formation of gas phase sulfur. For each mole of S volatilized, an additional mole of Na_2CO_3 is formed. If NaOH needs to be regenerated, one extra mole of $Ca(OH)_2$ is required for each mole of S volatilized.

$$Na_2CO_3 + Ca(OH)_2 \Rightarrow 2NaOH + CaCO_3 + H_2O \qquad [5]$$

When H_2S is absorbed into green liquor, $NaHCO_3$ is formed.

$$H_2S + Na_2CO_3 \Rightarrow NaHS + NaHCO_3 \qquad [6]$$

$$NaHCO_3 + Ca(OH)_2 \Rightarrow NaOH + CaCO_3 + H_2O \qquad [7]$$

The net impact is that for each mole of S devolatilized, one extra mole of $Ca(OH)_2$ is required as compared to conventional kraft pulping with a recovery boiler.

The increase of lime demand thus depends on the amount of sulfur volatilized during gasification, the pulping process and in which form sulfur is needed in it, and the efficiency of H_2S absorption. Increased lime demands for some scenarios are shown in Figure 2 through Figure 4 as a function of the fraction of the sulfur that is present in the product gas after the gasifier.

Figure 2 shows the increase in lime use for kraft pulping if H_2S is absorbed directly into green liquor. With 100% of S in the gas phase for low-temperature gasification, lime demand increases by close to 200% if the selectivity of H_2S absorption over CO_2 absorption is 10. For atmospheric and pressurized high temperature gasification, approximately 20% and 60% of S are in the gas phase, respectively. These correspond to lime demand increases of close to 40% and 115%. In all cases,but in particular with low-temperature gasification, the increase in lime demand is unacceptably high.

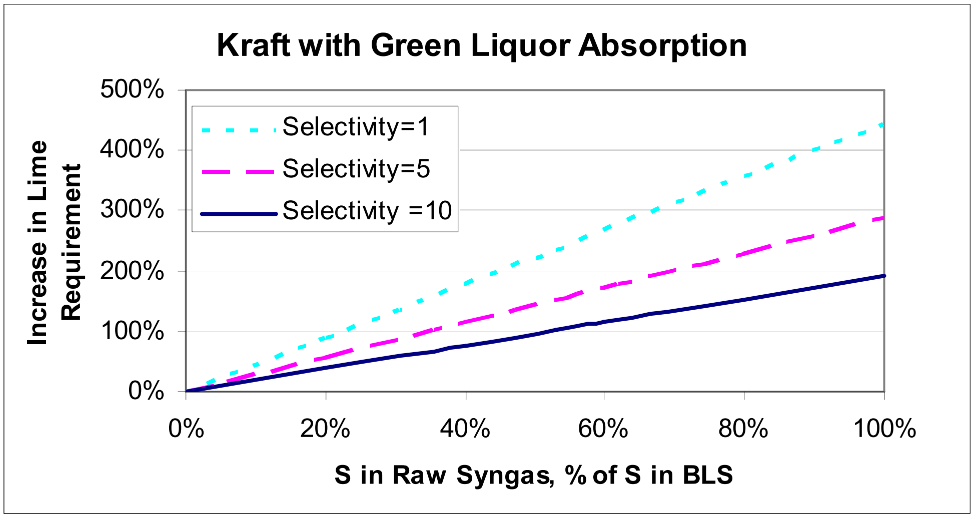

Figure 2. Increase in lime use for kraft pulping with direct green liquor absorption of H_2S from the gasifier product gas.

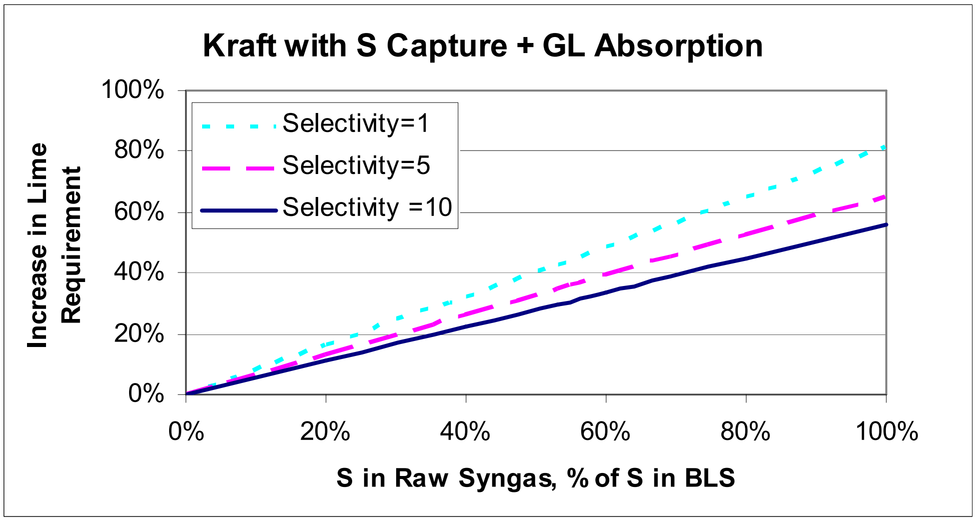

Figure 3. Increase in lime use for kraft pulping with green liquor absorption of gas containing 50% H_2S and 50% CO_2.

Figure 3 shows the corresponding increase in lime requirement for kraft pulping if H_2S is first captured and an H_2S-rich stream produced. The lime demand increases are now reduced, and are approximately 10% for atmospheric high-temperature gasification, 35%, for pressurized high-temperature gasification, and 55% for low-temperature gasification. These are still significant increases but substantially lower than if H_2S is absorbed directly from the product gas.

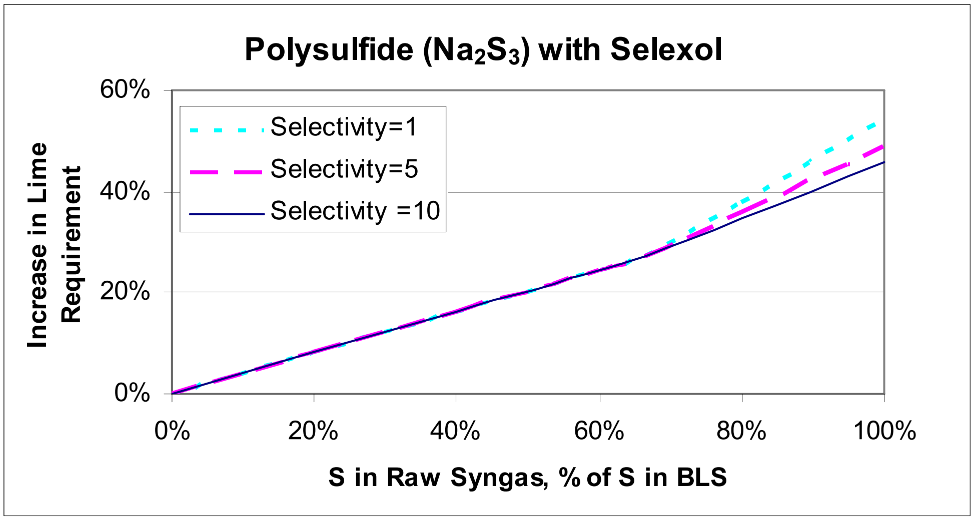

Figure 4. Increase in lime use for polysulfide pulping.

Figure 4 shows the increase in lime use for polysulfide pulping with the assumption that any sulfur in the gas phase of up to 67% is used in a Claus process for elemental sulfur production, and any gas phase S exceeding 67% of the total amount is captured by green liquor absorption from a concentrated stream. The increases in lime demand are 8%, 25%, and 45% for atmospheric and pressurized high-temperature gasification and low-temperature gasification. These numbers are lower than for kraft with absorption from a concentrated H_2S stream. This is because for up to 67% of S in the gas phase there is no H_2S absorption and associated increase in lime demand. Until 67% of S in the gas phase, the whole increase is due to extra Na_2CO_3 formed because of S volatilization.

MSSAQ pulping requires no NaOH, and hence the whole lime cycle can be eliminated with that pulping process integrated with gasification. For ASAQ pulping there will be an increase in lime demand because of both sulfur volatilization and co-absorption of CO_2 during absorption of SO_2 into the liquor.

Syngas Contaminants and Gas Cleanliness Requirements

Many of the processes for production of fuels from the syngas have very low tolerances for contaminants such as alkali metals, chlorine, ammonia, and tar. Due to the nature of black liquor several of these contaminants are present in the product gas from black liquor gasification, and may need to e removed from the syngas. These issues will be discussed more in the detail in the presentation.

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