Integration of a sulfite pulp mill and a viscose plant

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Hypothesis

- There are several benefits obtained if a dissolving pulp mill and a viscose fiber plant are built on the same site and ”connected”.
  - Lower chemical consumption (less waste)
  - Lower polluting emissions
  - Lower energy consumption
  - Lower production cost

The project is divided into the following cases:

- Prehydrolysis kraft pulping and viscose
- Sodium sulfite pulping and viscose
- Magnesium sulfite pulping and viscose
- Multi stage sulfite pulping and viscose
- Dissolving pulping and other fiber processes

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  - Appita 69(2016)3, 264-272
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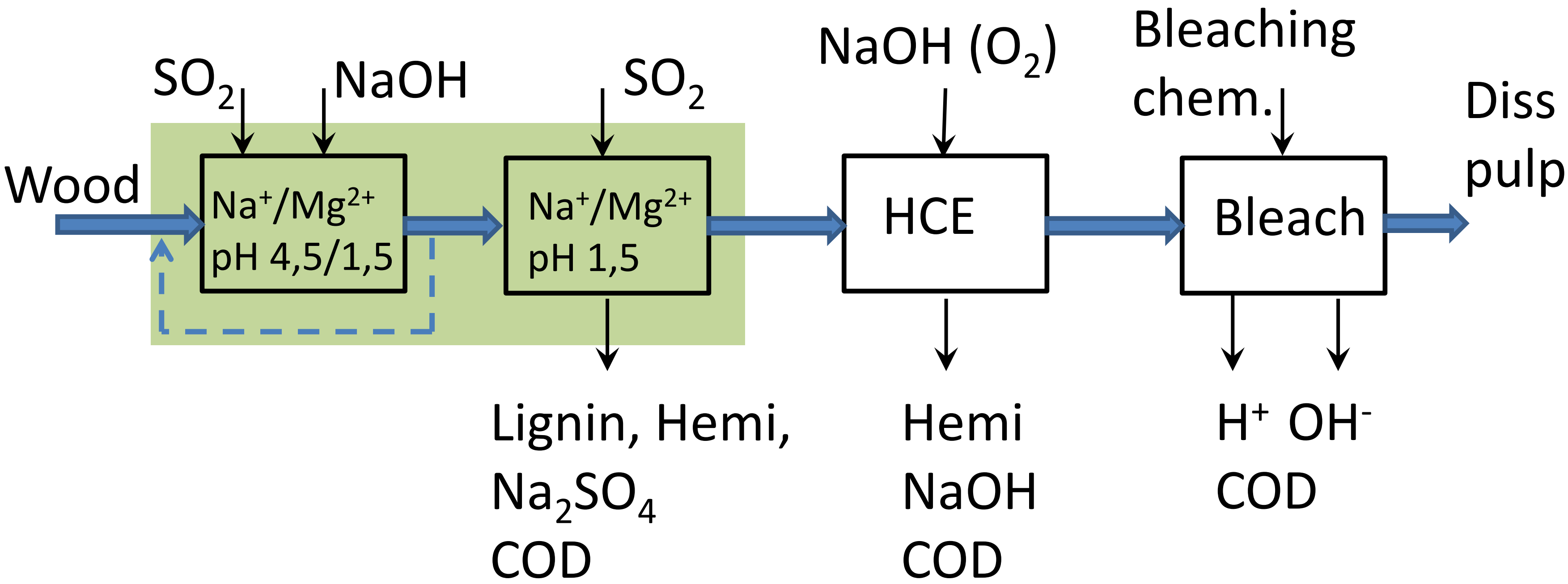
A sulfite dissolving pulp mill



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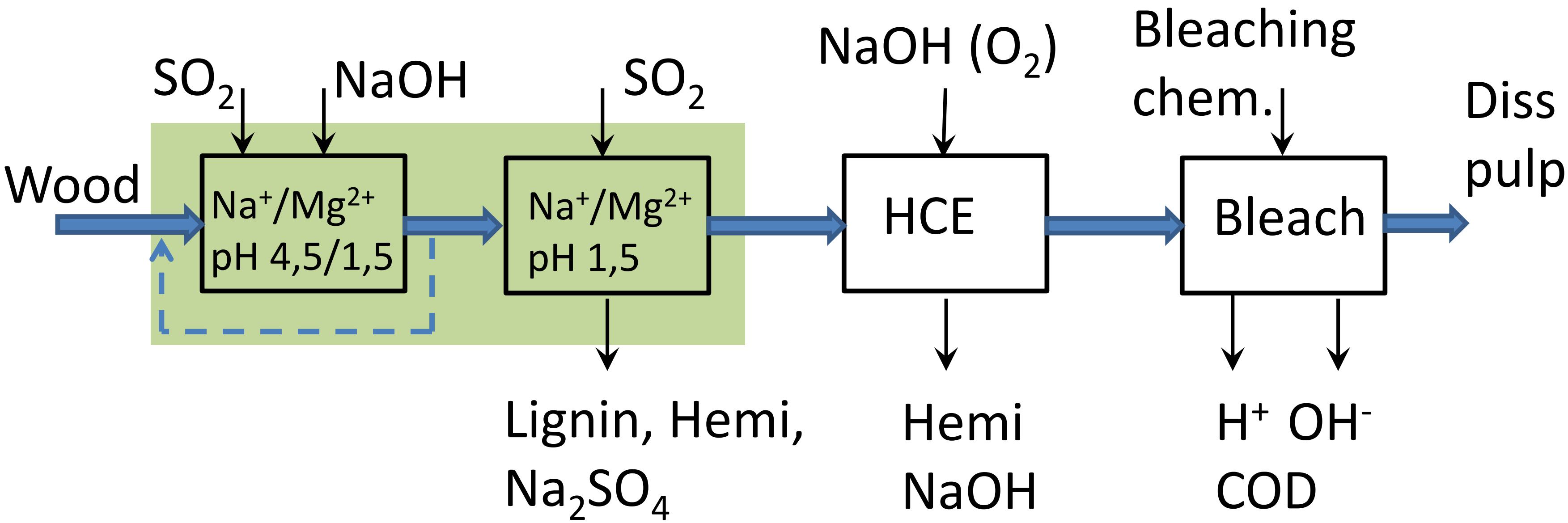

- The cooking base is either sodium or magnesium

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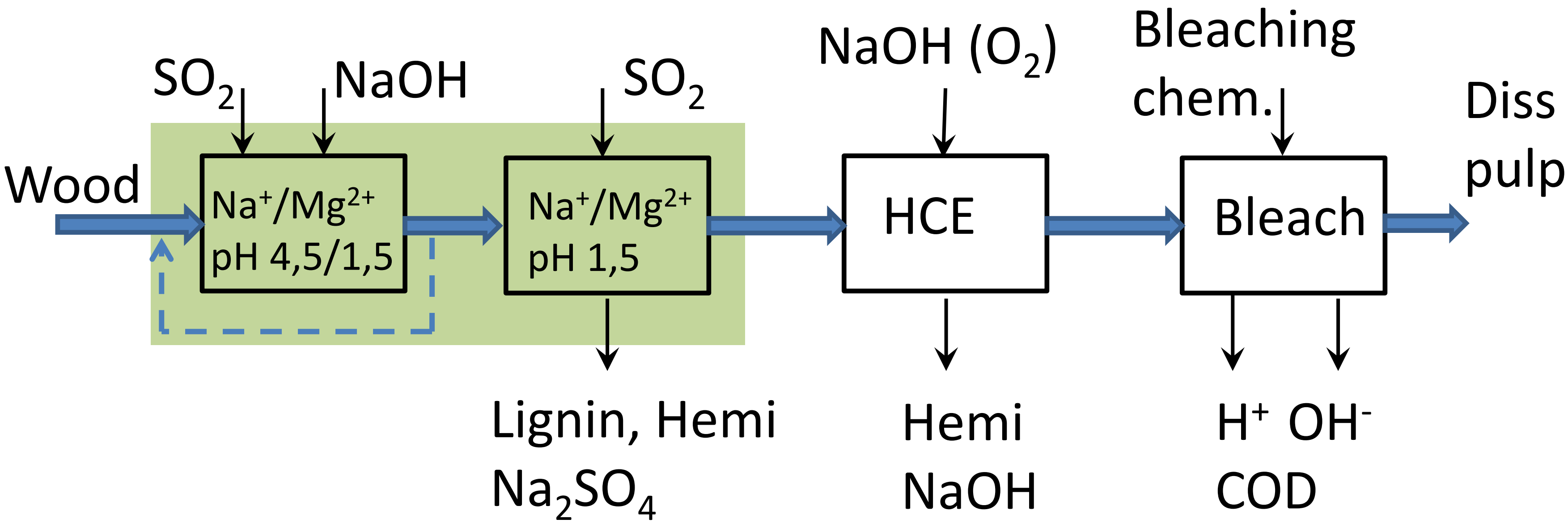

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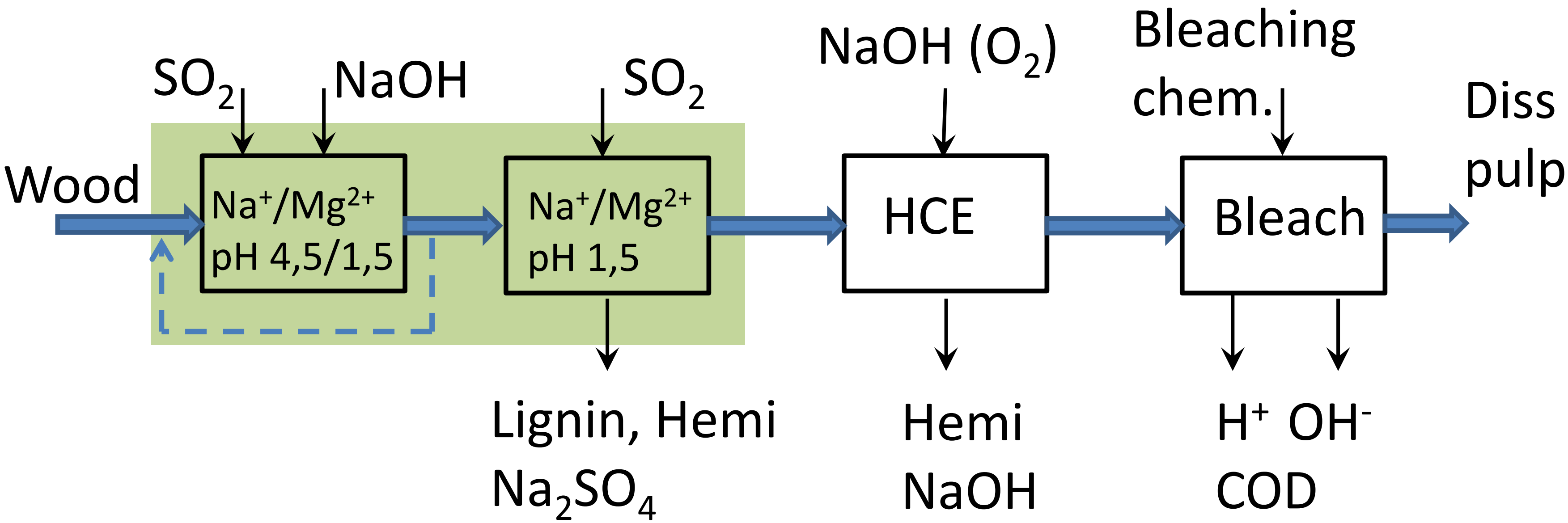

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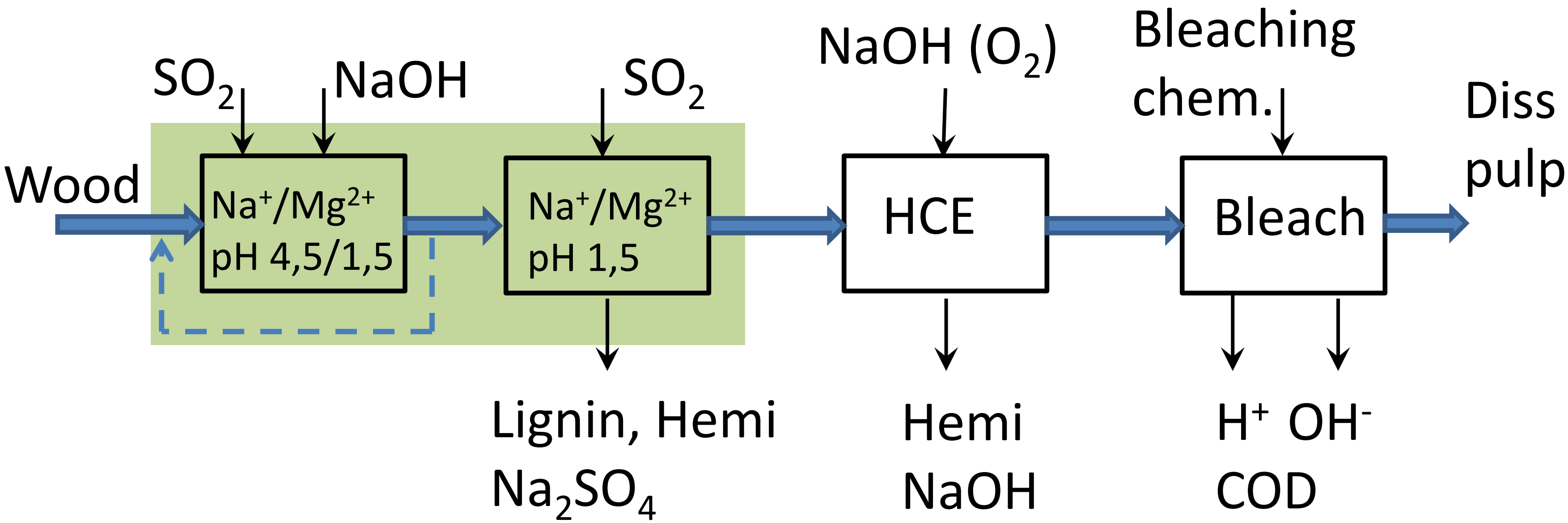

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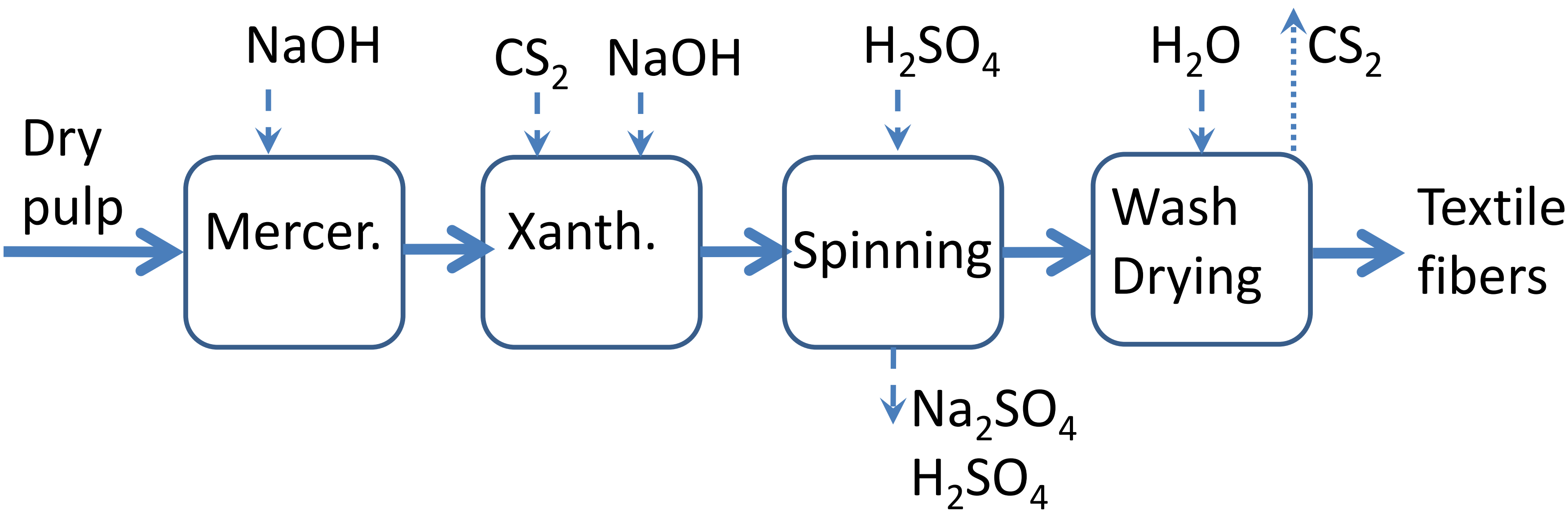
- Initial pH is 4,5 or 1,5. The rest of the cook is pH 1,5.
- Initial L/W ratio is high but reduced to 2,5/1 after puffing
- Bleaching is done in acidic and alkaline stages

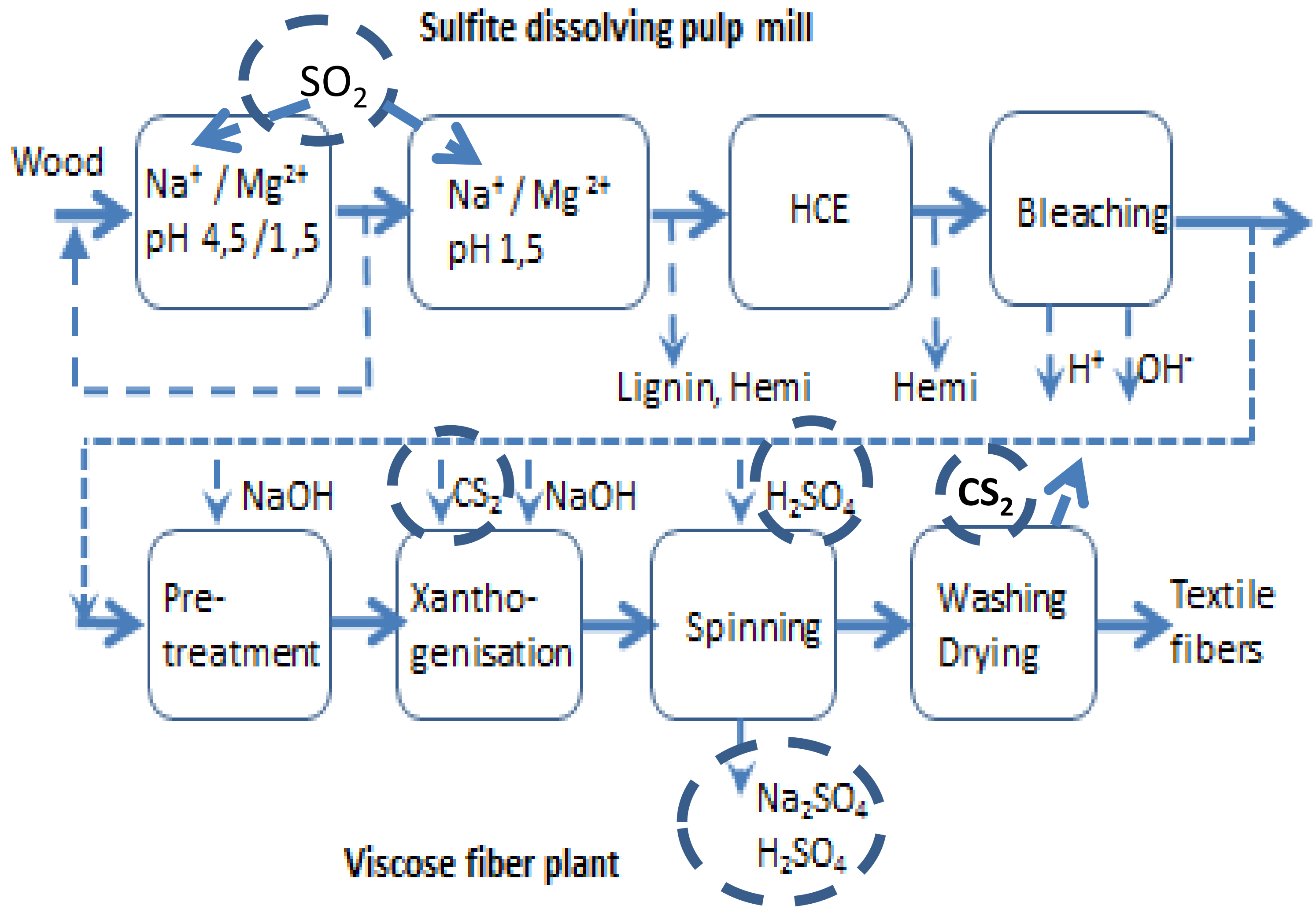
A viscose textile fiber plant



Sulfur based compounds in the two integrated plants

- SO_2
- CS_2
- H_2SO_4
- Na_2SO_4
- H_2S
- Na_2S
- S

Sulfur ”Mass balance”



Integration alternatives

- Wet pulp vs dry pulp
- On site production of CS_2
- On site production of H_2SO_4
- Reuse of Na_2SO_4 from viscose plant as make-up in the pulp mill.
- Avoid SO_2 and H_2S emissions and landfill of by-products

- *(1 t wood =1/3 t pulp =1/3 t viscose)*
- *(Swedish Rayon viscose plant)*

Steam saving in the pulp mill

- The dissolving pulp is only semi-dried after the pulp mill i.e. to about 40% dry solids.

- Steam saving (3 bar) about 3,3 GJ/ton of pulp

- (Based on GROT biofuel = 15€ /t)

Chemical Recovery in Na based sulfite pulp mills

- Stora Kopparberg method
- SCA Billerud method

- General
  - Spent liquor Sulfur compounds are incinerated and reduced to Sulfide.
  - Oxidized to SO_2 or reduced to elemental S and then oxidized to SO_2.
  - Dissolved in Na_2CO_3 and add SO_2.

Stora Kopparberg Sulfite recovey process

- Recovery boiler delivers:
  - Na_2CO_3 + Na_2S (recovery boiler similar to kraft)

  - $Na_2S + CO_2(g) \rightarrow H_2S\ (g)$
  - $2\ H_2S\ (g) + O_2 \rightarrow 2\ S + 2\ H_2O$
  - $S + O_2 \rightarrow SO_2\ (g)$
  - SO_2 +Na_2CO_3 solution → new cooking acid

SCA Billerud Sulfite recovery process

- Recovery Boiler delivers:
  - Na_2CO_3 + Na_2S (reducing conditions in boiler)
  - Cooler generates dust (Na_2CO_3 + C)

  - $Na_2S + CO_2 (g) \rightarrow H_2S (g) + Na_2CO_3$
  - $H_2S + 3/2\ O_2 \rightarrow SO_2 (g) + H_2O$
  - SO_2 dissolved in Na_2CO_3 solution $\rightarrow$ new cooking acid

Claus process

$2\ H_2S + O_2 \rightarrow 2\ S + 2\ H_2O$ (over all reaction)

Step 1 Thermal step (> 850 ^{o}C)

$2\ H_2S + O_2 \rightarrow 2\ SO_2 + 2\ H_2O$

Step 2 Catalytic step (heat, cat reaction (Al (III) or Ti (IV), cooling)

$2\ H_2S + SO_2 \rightarrow 3\ S + 2\ H_2O$

Production of CS_2 (bp 46 ^{o}C)

Modern, high efficiency process:

$CH_4 + S_4 \rightarrow CS_2 + 2\ H_2S$

(methane)

600 °C

20 ^{o}C

To viscose plant (Demand 150 kg CS_2/t)

To sulfite pulp mill (Claus process)

Older process using charcoal:

$C + 2S \rightarrow CS_2$

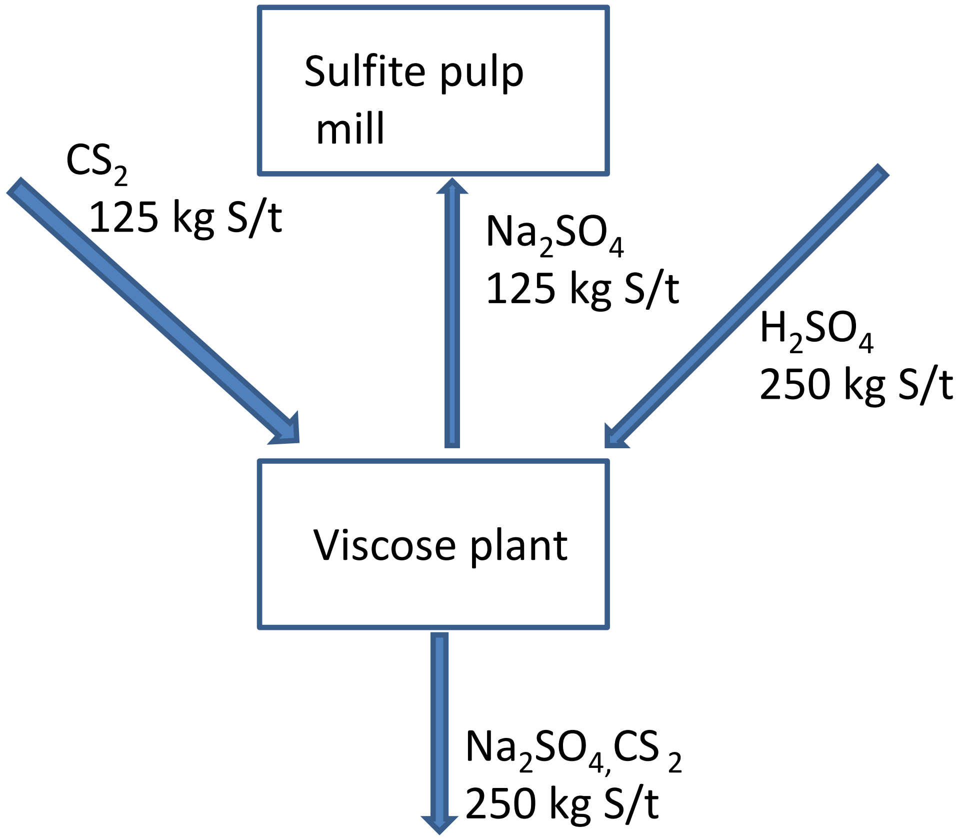
(850 °C)

H_2SO_4 process

- $S + O_2 \rightarrow SO_2$
- SO2 + O2 (V2O5, 1-2 bar, 450 C) → SO3
- SO3 + H2SO4 → H2S2O7
- H2S2O7 + H2O → 2 H2SO4

- Over all reaction:
- $2\ SO_2 + O_2 \rightarrow 2\ SO_3$ (450 ^oC, cat V_2O_5)

S-balance for an integrated dissolving pulp mill and a viscose plant (kg S/t)



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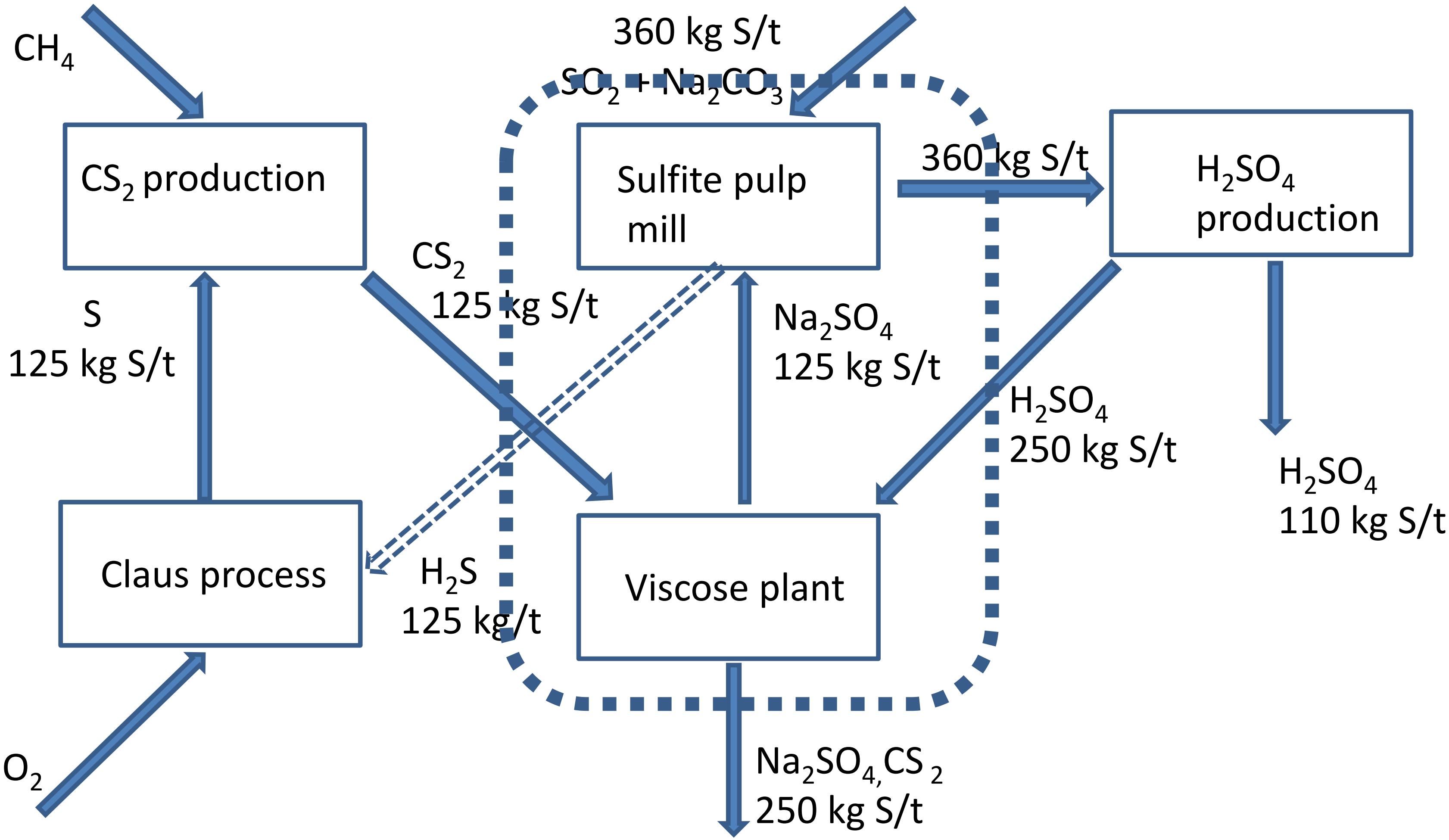

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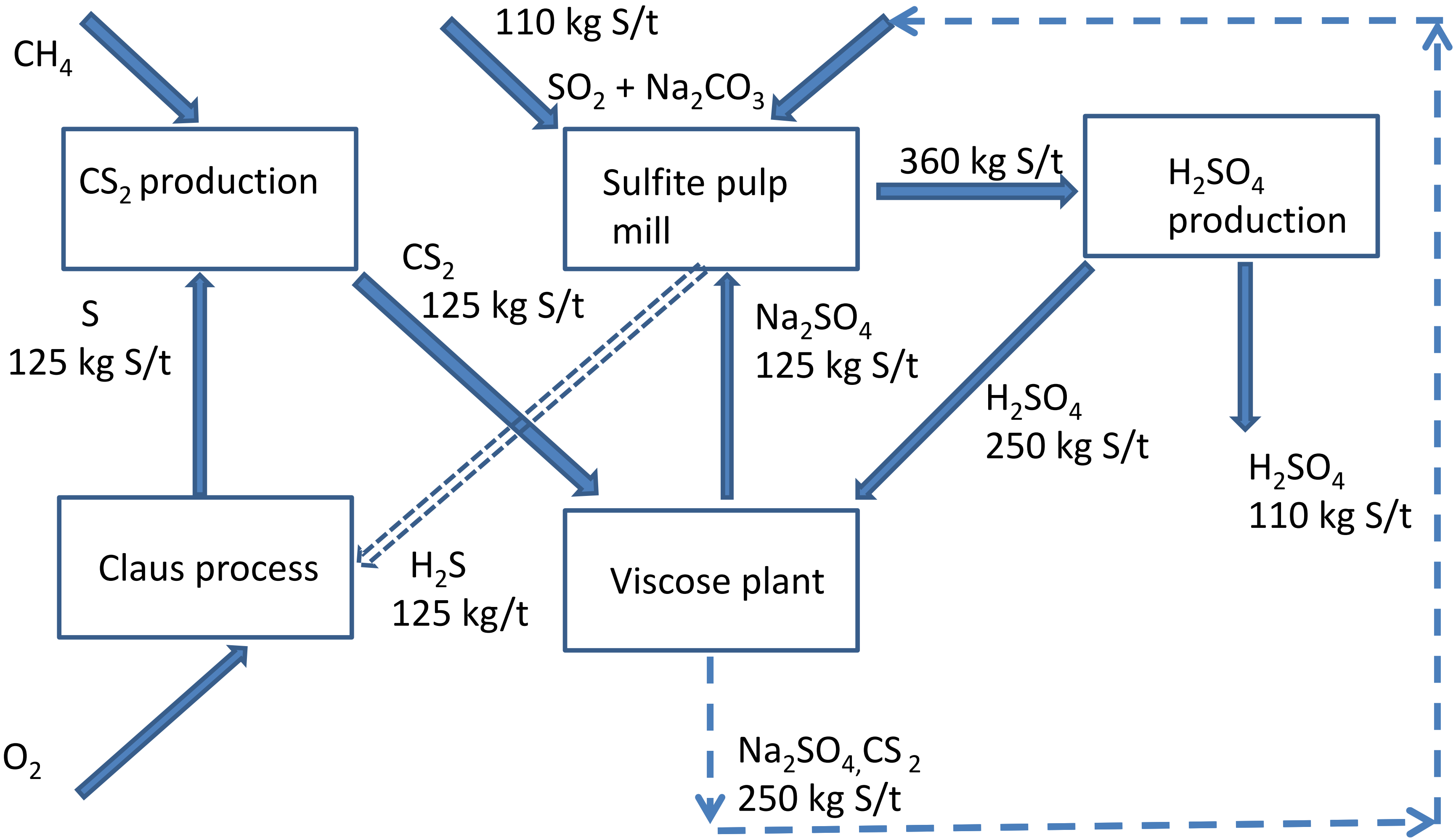
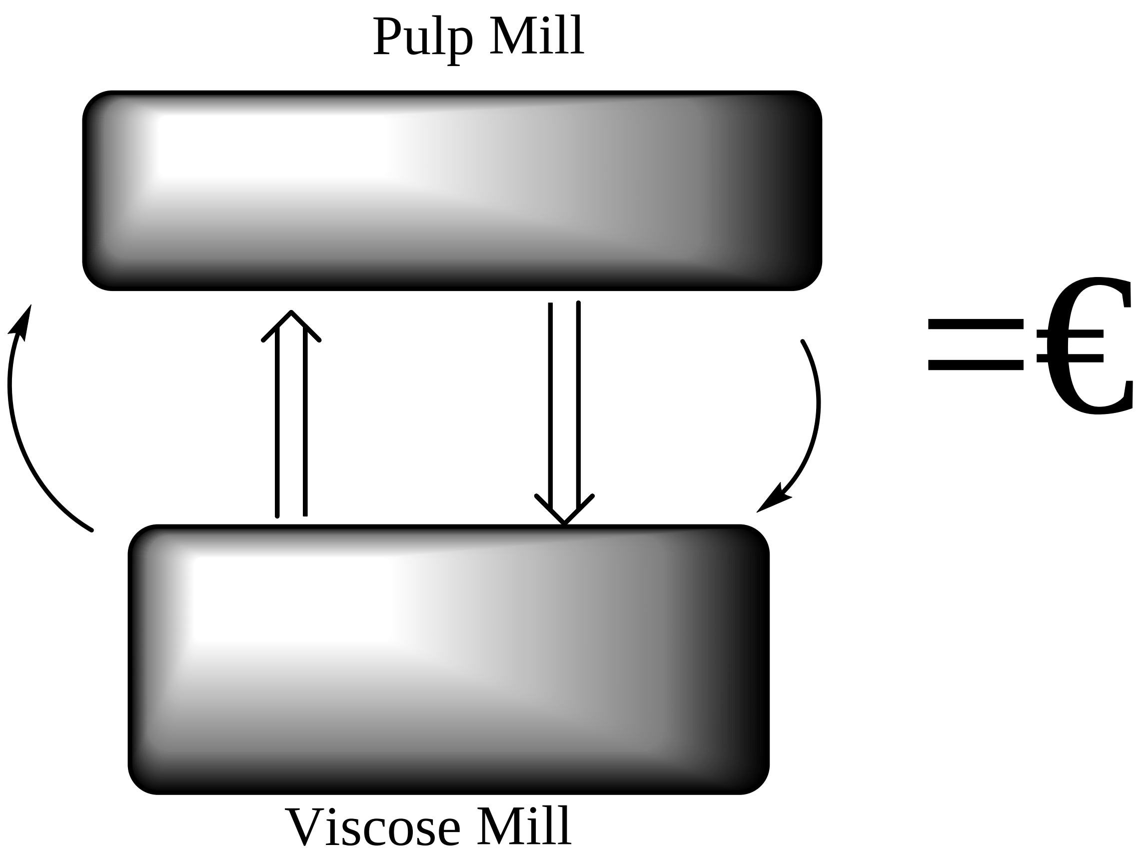


Conclusions

- Wet pulp can replace dried pulp in the viscose plant which saves steam.
- Internal CS_2 can be prepared from CH_4 and elemental S at high temperature (600 ^oC)
- The viscose by-product Na_2SO_4 can be reused as make up in the pulp mill.
- On site production of H_2SO_4 and CS_2 is beneficial

Basic idea.



Steam saving in the pulp mill

- The dissolving pulp is only semi-dried after the pulp mill i.e. to about 40% dry solids. Is it possible? Overflow in viscose mill?
- Steam saving (3 bar) about 3,3 GJ/ton of pulp
- (Based on GROT biofuel = 15€ /t)

Claus process

$2\,H_2S + O_2 \rightarrow 2\,S + 2\,H_2O$ (over all reaction)

Step 1a Thermal step (> 850 ^{o}C)

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Step 1b $2\,H_2S + SO_2 \rightarrow 3\,S + 2\,H_2O$

Step 2 Catalytic step (heat, cat reaction (Al (III) or Ti (IV), cooling)

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Reuse of by-product Na_2SO_4

The Na_2SO_4 by-product from the viscose plant can be concentrated by multi stage evaporation and then crystallization at low temp, centrifuged and finally semi or fully dried. This salt can be used as sulfur make-up in the sulfite pulp mill. Cf the Swedish Vargön sulfite pulp mill.

Consumed in Si-mill: 24% tot SO_2* → 360 kg S/t pulp

Available in viscose plant → 450-600 kg Na_2SO_4 /t pulp or 145 – 200 kg S/t pulp.**

*No puffing is performed **50% in spinn bath/50% with wet string

The Stora Kopparberg chemical recovery process

In the recovery boiler spent cooking acid is converted to *Na_2CO_3 and Na_2S*.
The sulfides are then converted to *H_2S* with the help of CO_2 .The H_2S is then either reacting with SO_2 to elemental *S* in a Claus process or oxidized with O_2 to *SO_2.* Elemental sulfur is oxidized to SO_2 with air and then dissolved in Na_2CO_3.
After addition of more SO_2 the cooking acid is ready for use.

The SCA Billerud chemical recovery process

- The recovery boiler is burning concentrated spent acid under reducing conditions to ”dust” (*Na_2CO_3 and carbon) and H_2S*. The H_2S is then incinerated with the undissolved dust and the generated *SO_2* is dissolved in the Na_2CO_3 solution. The cooking acid is ready for use.

S mass balance II
(kg S/ton pulp).

Into/ out of the viscose mill

- CS_2 30% & 50% recycle 150 kg CS2/ t
- H_2S0_4 750 kg/ t
- Tot S 125 + 250 = 375 kg S / t

- Na_2SO_4 550 kg/ t pulp = 125 kg S/ t
- CS2 to air 70 kg S/ t
- H2S to air 5 kg S/ t
- SO2 to air 5 kg S/ t
- S to landfill 30 kg S/ t
- To effluent treatment 140 kg S/ t
- Tot S 125+70+4+4+30 + 140 = 375 kg S/ t

Into the pulp mill

- (6% Tot SO2 & 4/1 & 35% yield)
- Tot S 60 x 4 x 3 x 32/64 = 360 kg S/ t pulp

Carbon disulfide, CS_2

- Boiling point : 46,3 °C
- Flash point: - 43 °C
- Lower explosion limit , LEL : 0,6 vol%; 19 mg/l
- Upper explosion limit, UEL : 60 vol%; 1900 mg/l