LIFE CYCLE ASSESSMENT STUDY OF A SULFURIC ACID MANUFACTURING PROCESS IN THE CHEMICAL PULPING INDUSTRY

Lappeenranta–Lahti University of Technology LUT

Master's Programme in Sustainability Science and Solutions, Master's thesis

2023

Martta Naukkarinen

Examiners: Professor, D.Sc. (Tech) Risto Soukka

Associate Professor, D.Sc. (Tech) Sanni Väisänen

Instructor: Senior Development Engineer, M.Sc. (Tech) Antti Pietiläinen

ABSTRACT

Lappeenranta–Lahti University of Technology LUT

LUT School of Energy Systems

Environmental Technology

Martta Naukkarinen

Life Cycle Assessment Study of a Sulfuric Acid Manufacturing Process in the Chemical Pulping Industry

Master's thesis

2023

101 pages, 16 figures, 15 tables and 4 appendices

Examiners: Professor Risto Soukka and Associate Professor Sanni Väisänen

Instructor: Senior Development Engineer Antti Pietiläinen

Keywords: life cycle assessment, sulfuric acid, kraft pulping, concentrated non-condensable gases, environmental impact

Sulfuric acid is one of the most used chemicals in the world and is mainly produced from by-product elemental sulfur from oil and gas refineries. Alternatively, sulfuric acid can be manufactured for example from side streams from metal refining or Kraft pulping. Utilizing side streams of pulping is a development trend in the pulping industry. This thesis was conducted for ANDRITZ and the aim was to study the environmental impacts of sulfuric acid production process from concentrated non-condensable gases at pulp mill. Life cycle assessment study was done with two version of the process: one that uses additional elemental sulfur input and another with only odorous gases. Startup of the plant and two electricity production methods were considered as different scenarios. The process without elemental sulfur had lower environmental impacts in all studied impact categories except for terrestrial eutrophication potential and water depletion potential. There was variation between the impact categories but main contributors to the environmental impacts were the production of elemental sulfur, electricity and process water. In many impact categories, the process that uses elemental sulfur had significantly higher impacts. The results of the baseline scenario were compared to two previous LCA studies of sulfuric acid production from elemental sulfur. The environmental impacts of this study were lower in almost all of the impact categories, but higher impacts were shown for terrestrial eutrophication potential and human toxicity potential. For the process without elemental sulfur, global warming potential was notably lower in comparison to the other version of the process and previous studies.

TIIVISTELMÄ

Lappeenrannan–Lahden teknillinen yliopisto LUT

LUT Energiajärjestelmät

Ympäristötekniikka

Martta Naukkarinen

Elinkaariarviointi rikkihapon valmistusprosessista kemiallisessa selluteollisuudessa

Ympäristötekniikan diplomityö

2023

101 sivua, 16 kuvaa, 15 taulukkoa ja 4 liitettä

Tarkastajat: Professori Risto Soukka ja apulaisprofessori Sanni Väisänen

Ohjaaja: Vanhempi kehitysinsinööri Antti Pietiläinen

Avainsanat: elinkaarianalyysi, rikkihappo, sulfaattisellun valmistus, väkevät hajukaasut, ympäristövaikutus

Rikkihappo on yksi maailman käytetyimmistä kemikaaleista ja pääosin sitä tuotetaan sivutuotteena öljyn ja kaasun jalostuksesta saatavasta alkuainerikistä. Vaihtoehtoisesti rikkihappoa voidaan tuottaa esimerkiksi metallinjalostuksen tai sulfaattisellun sivuvirroista. Sellunvalmistuksen sivuvirtojen hyödyntäminen on selluteollisuuden kehitystrendi. Tämä diplomityö tehtiin ANDRTIZille ja sen tarkoituksena oli tutkia sellutehtaan väkevistä hajukaasuista valmistetun rikkihapon tuotantoprosessin ympäristövaikutuksia. Ympäristövaikutusten arviointi tehtiin elinkaarianalyysilla prosessin kahdesta versiosta: yhdestä, jossa käytetään lisättyä alkuainerikkiä ja toisesta, jossa käytetään vain väkeviä hajukaasuja. Tutkimuksessa huomioitiin myös tehtaan käynnistys sekä kaksi eri sähköntuotantomenetelmää eri skenaarioissa. Prosessilla, jossa ei käytetä alkuainerikkiä, oli alhaisemmat ympäristövaikutukset kaikissa muissa tutkituissa vaikutusluokissa paitsi maaperän rehevöitymisessä ja veden ehtymisessä. Eri skenaarioiden välillä oli eroja, mutta suurin vaikutus oli alkuainerikin, sähköntuotannon ja prosessiveden valmistuksella. Perusskenaarion tuloksia verrattiin aiemmin tehtyihin elinkaarianalyyseihin, jossa rikkihappo valmistettiin alkuainerikistä. Tämän tutkimuksen ympäristövaikutukset olivat alhaisemmat useimmissa vaikutusluokissa, mutta suurempia vaikutuksia oli maaperän rehevöitymiselle ja ihmiselle myrkyllisyydelle. Prosessilla, jossa ei käytetä alkuainerikkiä, ilmaston lämpenemisen potentiaali oli merkittävästi pienempi kuin prosessin toisessa versiossa ja muissa tutkimuksissa.

ACKNOWLEDGEMENTS

First, I would like to thank ANDRITZ for giving me this opportunity to work on such an interesting topic. Thank you to my instructor Antti Pietiläinen for all the help and guidance as well as to everyone at ANDRITZ who provided the information needed in this study. I want to thank my examiners Risto Soukka and Sanni Väisänen for their comments, feedback and answers to my questions. A special thank you to my friends and family for supporting and encouraging me during this whole process!

Lappeenranta, 24 January 2023

Martta Naukkarinen

SYMBOLS AND ABBREVIATIONS

Roman characters

m	mass	[kg, t]
n	amount of substance	[mol]
V	volume	[m^3, Nm^3]
E	energy	[MJ]
	heating value	[MJ/kg]
	standard volume	[Nm^3/kg]

Greek characters

ρ	density	[kg/m^3]

Chemical symbols

1,4-DB	1,4-Dichlorobenzene
Al	Aluminum
$Ca(OH)_2$	Calcium hydroxide, slaked lime
$CaSO_4$	Calcium sulfate
$(CH_3)_2S$	Dimethyl sulfide
$(CH_3)_2S_2$	Dimethyl disulfide
CH_3SH	Methyl mercaptan
CH_4	Methane
ClO_2	Chlorine dioxide
Cu	Copper

CuS	Copper sulfide
Fe	Iron
FeO	Iron oxide
FeS_2	Iron sulfide
$FeSO_4$	Iron sulfate
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulfide
H_2SO_3	Sulfurous acid
H_2SO_4	Sulfuric acid
$H_4Na_2O_{12}S_3$	Sodium sesquisulfate
MeOH	Methanol
$MgSO_4$	Magnesium sulfate
$MnSO_4$	Manganese sulfate
NaOH	Sodium hydroxide, caustic soda
Na_2S	Sodium sulfide
Na_2SO_3	Sodium sulfite
Na_2SO_4	Sodium sulfate
N_2O	Nitrous oxide
NOx	Nitrogen oxides
PbS	Lead sulfide
O_2	Oxygen
O_3	Ozone
S	Sulfur

Sb	Antimony
SO_2	Sulfur dioxide
SO_3	Sulfur trioxide
SO_4	Sulfate
V	Vanadium
V_2O_5	Vanadium pentoxide
ZnS	Zinc sulfide

Abbreviations

ADP	Abiotic resource Depletion Potential
ADt	Air Dry Ton
AP	Acidification Potential
CNCG	Concentrated Non-Condensable Gas
CTUh	Comparative Toxicity Unit for humans
DNCG	Diluted Non-Condensable Gas
EF	Environmental Footprint
eq	Equivalent
EP	Eutrophication Potential
ESP	Electrostatic Precipitator
GAP	Generator Acid Purification
GHG	Greenhouse Gas
GWP	Global Warming Potential
HTP	Human Toxicity Potential
HVAC	Heating, ventilation, and air conditioning

LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
NCG	Non-Condensable Gas
ppm	Parts Per Million
SC	Scenario
SOG	Stripper Off-Gases
TRS	Total Reduced Sulfur
WDP	Water Depletion Potential
WSA	Wet-gas Sulfuric Acid

Table of contents

Abstract

Acknowledgements

Symbols and abbreviations

Appendices

Figures

Tables

1. Introduction

Humans are facing multiple environmental issues at a global, planetary level (Steffen et al. 2015, 737). Of the nine planetary boundaries defining the environmental limits for humans to develop on (Steffen et al. 2015, 737), at least four have been crossed due to human activities (SYKE 2018). They include climate change, nutrient flows causing eutrophication, biodiversity loss and land-system change (SYKE 2018). Persson et al. (2022, 1510) and Wang-Erlandsson et al. (2022, 380) say that also the boundaries of novel entities and freshwater use have been exceeded. The planetary boundaries have been transgressed because of increasing industrial activity and economic development (Rockström et al. 2009, 2 & 20).

In Finland, the pulp and paper industry is an important part of the economy (Back 2019) accounting for about 14 % of export (Elinkeinoelämän keskusliitto 2022). The pulp and paper industry has been a major contributor to emissions and pollution as well as to energy and natural resource use. In the last years, technological improvements and environmental management of the pulping processes, have led to decrease of emissions and energy consumption (Suhr et al. 2014, 24). In spite of the progress in environmental sustainability (Suhr et al. 2014, 25) and due to tightening environmental regulations (Mahecha-Botero et al. 2021, 100), it is important to continue making environmentally clever improvements to the pulp production (Suhr et al. 2014, 25). Current challenges of the pulping industry include making the chemical circulation of pulp mills more closed (Mahecha-Botero et al. 2021, 100), the collection and handling of odorous gases from the pulping process (Hovikorpi & Vakkilainen 2019, 297) and reducing the pulp mill emissions to water (Suhr et al. 2014, 31).

One of the pulping industry’s development trends is the utilization of side streams of the pulping process and turning them into valuable by-products (Valmet 2017, 2). One possibility of side stream utilization is producing sulfuric acid from the sulfur rich odorous gases from a pulp mill process (Mahecha-Botero et al. 2021, 101). Odorous gases are nowadays at low concentrations due to development of collection and destruction technologies, but they can still cause issues (Suhr et al. 2014, 244). To produce sulfuric acid, odorous gases could be led to a plant integrated to a pulp mill (Mahecha-Botero et al. 2021, 100).

Sulfuric acid is produced largely from elemental sulfur by-product of oil and gas refining (King et al. 2013, 13). Because of the decarbonization of the energy system and shift from fossil fuels to renewable energy due to climate change, the production of oil and gas is decreasing. This would mean a decline of the by-product sulfur that is needed to produce sulfuric acid. The issue is not yet recognized because sulfur is considered to have abundant reserves and its price is low. Due to the growing demand of sulfur and sulfuric acid the problem is, however, critical and there is a need for new sources of sulfur. (Maslin et al. 2022, 1-2 & 6.)

Sulfuric acid production plants emit sulfur dioxide, nitrogen oxide, nitrous oxide, particulate matter and volatile organic emissions as well as some other pollutants. In addition to sulfur emissions, contributors to acid rain formation are nitrogen oxides which also cause human health problems and global warming. Other greenhouse gases contributing to climate change are nitrous oxide (USEPA 2022) and carbon dioxide emissions (Satein 2009, 1). In sulfuric acid plant carbon dioxide emissions are caused for example by the production of needed energy (McLean et al. 2022, 658). It is important to assess the emissions of sulfuric acid production in order to comprehensively understand the environmental impacts of the process (Adeniran et al. 2017, 2). The evaluation of environmental impacts can be done with life cycle assessment (LCA) (McLean et al. 2022, 655).

There is a lack of life cycle assessment studies of sulfuric acid production. According to McLean et al. (2022, 656) there are limited amount of LCA studies done on sulfuric acid plants even though there have been efforts of incorporating LCAs in related industries. Only a few assessments have been conducted studying the manufacturing of sulfuric acid (Adeniran et al. 2017). Marwa et al. (2017) studied the environmental impacts of sulfuric acid production from elemental sulfur in a sulfuric acid plant located in Tunisia and Adeniran et al. (2017) in a plant located in Nigeria. An LCA study from McLean et al. (2022) consisted of a comparison of metal smelter sulfuric acid plant with and without a heat recovery system.

This study however, had a system boundary so different from the other two studies that it is not comparable.

A couple of other LCA studies related to the production of sulfuric acid have also been executed but they are not directly comparative to the others as they either don’t separate the environmental impacts of sulfuric acid from co-generated products or assess the impacts from the point of view of disposal rather than production. Wu et al. (2020) conducted an LCA of co-generation of cement and sulfuric acid. Intang et al. (2019) studied the environmental impacts of spent sulfuric acid form lead-acid batteries from the perspective of discharging the spent sulfuric acid to the environment.

1.1. Objectives and limitations

This study is conducted for ANDRITZ whose motivation for the study is to utilize side streams of a kraft pulp mill in order to improve the environmental sustainability, cost savings and additional revenues (ANDRITZ GROUP 2022b). The objective of the study is to assess the environmental impacts of a sulfuric acid manufacturing process in the chemical pulping industry and compare them to the environmental impacts of alternative ways of producing sulfuric acid. The research questions of the study are following:

- What are the impacts of sulfuric acid manufacturing process in a Kraft pulp mill on climate change, acidification, eutrophication, water scarcity, abiotic resources and human toxicity?
- How do the environmental impacts differ for a process with and without additional elemental sulfur?
- How do the environmental impacts compare to the environmental impacts studied in previous life cycle assessment studies of alternative sulfuric acid manufacturing processes?

The study focuses on Wet-gas Sulfuric Acid process which utilizes odorous gases from Kraft pulping process as the sulfur input for the production of sulfuric acid. Two versions of the process are modelled: one with additional elemental sulfur input and one without it. The environmental impact categories studied are global warming potential, acidification potential, freshwater and terrestrial eutrophication potential, water depletion potential, abiotic resource potential of minerals and metals as well as energy carriers and carcinogenic and non-carcinogenic human toxicity potential.

The comparison of environmental impacts of different sulfuric acid manufacturing methods is done by evaluation where the results of this study are compared to results of previous studies. From the alternative methods of producing sulfuric acid, only the production from elemental sulfur is taken into account. This is because there aren't existing LCA studies in the literature that can be used in the comparison. The production methods excluded from the comparison are metal sulfide smelting, the regeneration of spent sulfuric acid and the sulfate roasting.

1.2. Methodology and structure

This thesis consists of a theoretical and empirical part. The theoretical part of the thesis is conducted as a literature review and consists of three main topics of which sulfuric acid market is examined first. After that, the Kraft pulping process, the sulfur balance and the odorous gases of Kraft pulping are presented. The last chapter of the theoretical section deals with sulfuric acid manufacturing processes. First the sulfuric acid production process is introduced generally and then different production methods, including the process at pulp mill, are presented.

After the theoretical part is the empirical part of the thesis which is a life cycle assessment study. LCA is a method for addressing environmental performance and impacts of a product through its life cycle and can be used as a tool for example, for recognizing improvement possibilities of environmental aspects and for marketing (ISO 14040, V). The LCA is conducted with GaBi Solutions LCA software and reported according to ISO standards 14040 and 14044. The LCA part of the thesis begins with goal and scope definition, then goes through life cycle inventory (LCI) and life cycle impact assessment (LCIA) and finally presents the results in life cycle interpretation. The results are then analysed and compared to alternative systems in the discussion chapter. In the last chapters, conclusions and summary are presented.

2. Sulfuric acid market

Sulfuric acid is a strong acid and in a liquid form it is oil-like, odorless (Kekkonen et al. 2013, 33), dense and clear (King et al. 2013, 1). Sulfuric acid dissolves completely to water and is corrosive for example, to aluminum and copper as well as skin. In soil and water, sulfuric acid causes acidification. Because of the acid nature, sulfuric acid is harmful to humans, other living organisms and ecosystems (Kekkonen et al. 2013, 33). In the nature, sulfuric acid forms from sulfuric dioxide in the atmosphere (Martin 2014, 4).

Sulfuric acid is one of, if not the most used chemicals in the world (Nleya et al. 2016, 19). It is also the cheapest inorganic acid (Nleya et al. 2016, 19) and due to its multiple applications in different industries, it has a significant importance as an industry chemical (Martin 2014, 2-3). Sulfuric acid market is a growing market with increase of consumption every year (Nleya et al. 2016, 19). The global production volume of sulfuric acid was 257 million tons in 2020 and is forecasted to grow to 295 million tons in 2026. (Fernandez 2021, 2). Maslin et al. (2022, 1) estimate that the annual use of sulfuric acid could grow to 400 million tons by 2040.

The largest market share of sulfuric acid is in Asia Pacific (Athen Information Solutions Pvt. Ltd. 2020, 1; King et al. 2013, 15). Following Asia Pacific, North America and Europe are the second biggest contributors to sulfuric acid markets. North America will likely grow at a considerable rate whereas European markets have reached their equilibrium. Mature European markets are due to the consumption of raw materials, awareness in environmental issues and technological development. Asia, however, is expected to continue to dominate the market. (Focus on Catalysts 2019, 2.) That is because of the increase in domestic demand (Athena Information Solutions Pvt. Ltd. 2020, 1).

The value of the global sulfuric acid market was 11.4 billion $ in 2017 and is expected to grow reaching 12.7 billion $ in 2024. The growth in sulfuric acid market is forecasted because of increase in population and new demand in emerging markets. Population growth drives the increasing demand for food crops, better infrastructure and base metals. (Athena Information Solutions Pvt. Ltd. 2020, 1.) In developing countries, the switch to foods with higher nutrient content, increases the demand for fertilizer use and thus sulfuric acid (Nleya et al. 2016, 19). Growth in using electric vehicles and batteries might also increase the demand for sulfuric acid (Maslin et al. 2022, 3). Emerging sulfuric acid markets are in China, India, Middle East (Athena Information Solutions Pvt. Ltd. 2020, 1) and Africa (Nleya et al. 2016, 19).

One of the market drivers of sulfuric acid is its large variety of applications (Athena Information Solutions Pvt. Ltd. 2020, 1) as both raw material and processing agent (Martin 2014, 2). The utilization of sulfuric acid has developed from ancient use as fabric bleaching and medicine to material in buildings and explosives. Today, sulfuric acid is mostly used as a process chemical rather than being in the product. (Maslin et al. 2022, 5.) It is used in various industries including fertilizer industry, mining industry, pharmaceutic industry and paper and pulp industry (Nleya et al. 2016, 19). Table 1 presents some industries and applications of sulfur acid.

The biggest market for sulfuric acid is the fertilizer industry (Benvenuto 2015, 5). Phosphate fertilizers are the most significant product in the market, taking up about 60 % of the global sulfuric acid consumption (Nleya et al. 2016, 19; King et al. 2013, 13). Important uses of sulfuric acid are also in petroleum refining, metal processing (Benvenuto 2015, 5), lithium-ion batteries and electric motors (Maslin et al. 2022, 1). Sulfuric acid is used as a catalyst in various industrial processes. For example, sulfuric acid as a catalyst is needed in the production of jet fuel, gasoline (King et al. 2013, 47) and nylon in the chemical industry (Athena Information Solutions Pvt. Ltd. 2020, 1).

Table 1. Industries and applications of sulfuric acid market.

Industry	**Application**	**Source**
Fertilizers	Phosphate fertilizer production, other fertilizer production	Nleya et al. 2016, 19; Benvenuto 2015, 5; King et al. 2013, 13
Mining industry	Ore leaching, ore oxides, mineral processing	King et al. 2013, 13; Nleya et al. 2016, 19; Athena Information Solutions Pvt. Ltd. 2020, 1
Metal industry	Metal processing, steel making, hydrometallurgy	Benvenuto 2015, 5; Nleya et al. 2016, 19
Oil refining industry	Petroleum refining, gasoline	Benvenuto 2015, 5; King et al. 2013, 13; Nleya et al. 2016, 19
Batteries	Lead acid batteries, lithium-ion batteries	Benvenuto 2015, 5; Maslin et al. 2022, 1
Water	Wastewater treatment, water treatment	Athena Information Solutions Pvt. Ltd. 2020, 1; Nleya et al. 2016, 19
Pharmaceutic industry	Pharmaceuticals	Nleya et al. 2016, 19; Athena Information Solutions Pvt. Ltd. 2020, 1
Paper industry	Pulp and paper production, paper bleaching, cellulose fibers	King et al. 2013, 13; Nleya et al. 2016, 19
Chemical industry	Chemical production, coloring agents	Benvenuto 2015, 5; King et al. 2013, 13; Nleya et al. 2016, 19
Other	Explosives, nuclear fuel processing	Maslin et al. 2022, 5

The production of sulfuric acid is so inexpensive that usually sulfuric acid is not recycled and rather the waste streams are neutralized (Benvenuto 2015, 12). The neutralization is done as direct neutralization with limestone or ammonia water (Song et al. 2013, 1558). Direct neutralization, however, has some problems such as disposal challenges of the waste sludge that is produced in the process as well as the removal of the value of the acid. If recovered, the acid value could be utilized. Because of the issues of neutralization and the possibility to gain economic and environmental benefits, multiple recovery methods have been attempted to develop. (Nleya et al. 2016, 19; Song et al. 2013, 1558.) Especially in Kraft pulping, the recovery would be feasible as the process scale is big enough (Benvenuto 2015, 12). Some recovery methods, their applications, advantages and disadvantages are shown in table 2.

Table 2. Sulfuric acid recovery methods (Nleya et al. 2016, 20).

Method	**Applications**	**Advantages**	**Disadvantages**
Rectification	Waste acid solutions, toluene nitration waste solution	Recovery of high purity acid	High energy consumption, high operation cost
Solvent extraction	Aqueous solutions, acid mine drainage	Suitable for large volumes and high concentrations, clean acid product	Hazardous chemicals, pre-treatment required
Crystallization	Waste pickling solutions, acid mine drainage	Low cost	High energy consumption, risk of scale formation
Acid retardation	Aqueous solutions, metal sulfate solutions, acid mine drainage	Low operation cost, high acid recovery, small equipment size	High consumption of fresh water, dilute acid product
Membrane technologies	Metallurgical plant effluents, aluminum surface processing solution, acid leach solution, diamond manufacturing waste solution, acid mine drainage, rare earth sulfate solutions	High acid recovery, clean acid product, low pay back period	High operation cost, not efficient at low acid concentration, membrane fouling

The membrane technologies include diffusion dialysis, electrodialysis, membrane distillation, membrane electrolysis and anion/cation exchange membranes (Nleya et al. 2016, 20). Other methods are ion exchange and oxidative degradation. In many of these methods, the purpose to extract either metals or organic compounds from the waste acid. (Song et al. 2013, 1558.) Recycling of sulfuric acid would be helpful in fulfilling the increasing demand. In addition to recycling of sulfuric acid itself, the recycling of the products where it is needed could help reduce the demand. These products could be for example, phosphate fertilizers, lithium-ion batteries and vehicle tires with rubber. (Maslin et al. 2022, 4-5.)

3. Sulfur in Kraft pulping

Sulfur is an important element needed in Kraft pulping process and it exists in the process in various forms. Sodium hydroxide (NaOH) and sodium sulfide (Na_2S) are the main chemicals as they are used cooking chemicals (Mahecha-Botero et al. 2021, 100; Alen 2015, 95; Polowski et al. 2006, 291). Other sulfur containing chemicals of the process include makeup chemicals such as sodium sulfate (Na_2SO_4) and sulfur compounds replacing them, like H_2SO_4 (Mahecha-Botero et al. 2021, 100). Emissions from the Kraft process also contain sulfur: SO_2 as emissions from boilers and different sulfide compounds in odorous gases (Hovikorpi & Vakkilainen 2019, 297 & 301).

This chapter focuses on the sulfur in Kraft pulping. First the Kraft pulping process is introduced. Next, the sulfur balance of Kraft pulping and ways of controlling it are presented. Then the sulfur containing Non-Condensable Gases released from the process as well as their treatment methods are discussed.

3.1. Kraft pulping process

Kraft pulping is a chemical pulping process where the aim is to produce cellulose fibers from wood or other feedstocks. In chemical pulping processes, fibrous matter is treated with aqueous and acid solutions to free the fibers by removing the lignin that is binding them. (Alen 2015, 95; Polowski et al. 2006, 291.) Chemical pulping is dominated by two pulping processes from which Kraft pulping is the most used method (Polowski et al. 2006, 291). Kraft pulping is also the overall leading technology in the pulp and paper industry (Bijok et al. 2022, 1, Polowski et al. 2006, 291) with 80 % of the world’s pulp production being from Kraft process (Suhr et al. 2014, 195). Kraft pulping is mature and well-established pulping technology with a versatility in wood utilization as it is possible to use both soft- and hardwood and different species as a feedstock (Bijok et al. 2022, 1). The benefits of Kraft pulping also include the recovery of used chemicals and thermal energy that can be utilized in the process (Alen 2015, 95) as well as the great pulp properties (Suhr et al. 2014, 195).

In Kraft process, the delignification of feedstock fibers is done using white liquor that contains cooking chemicals sodium hydroxide ($NaOH$) and sodium sulfide (Na_2S) (Mahecha-Botero et al. 2021, 100; Alen 2015, 95; Polowski et al. 2006, 291). The cooking of the feedstock matter is done at an elevated pressure and temperature (Polowski et al. 2006, 291) and alkaline conditions. (Alen 2015, 95). Kraft pulping consists of fiber line, also called pulp line, and recovery line (Suhr et al. 2014, 196; ANDRITZ n.d.) as seen in figure 1 (ANDRITZ n.d.). Other necessary systems like bleaching chemicals making and power generation are in connection with the main process lines (Suhr et al. 2014, 196). The flow chart of pulping liquors is presented in figure 2.

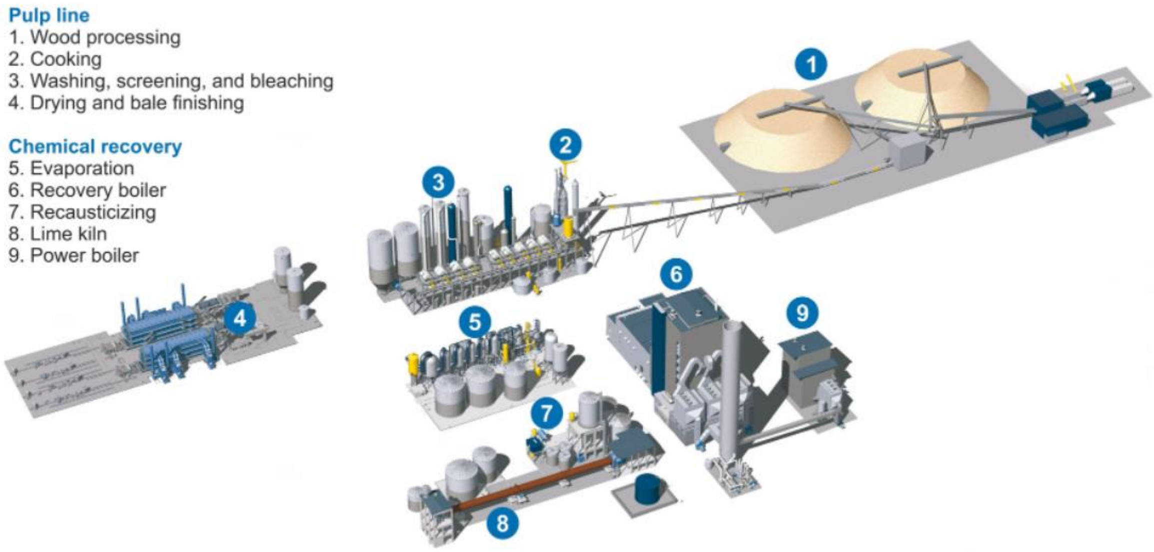


Figure 1. Kraft pulping process (ANDRITZ n.d.).

Fiber line includes the production of pulp from wood handling to pulp finishing. In wood handling, which is done before the cooking process, the feedstock wood goes through bark removing, chipping and screening stages. The processes of pulp production contain cooking, washing and screening, oxygen delignification, bleaching, and drying. (Suhr et al. 2014, 196-203.) The delignification of the wood fibers happens during the cooking in a digester where the organic matter of wood dissolves releasing the fibers and forming pulp and black liquor (Alen 2015, 95). After the cooking are the washing, screening, oxygen delignification, bleaching and drying stages of the pulp where the pulp properties like brightness and strength are achieved and pulp finished (Suhr et al. 2014, 199-203).

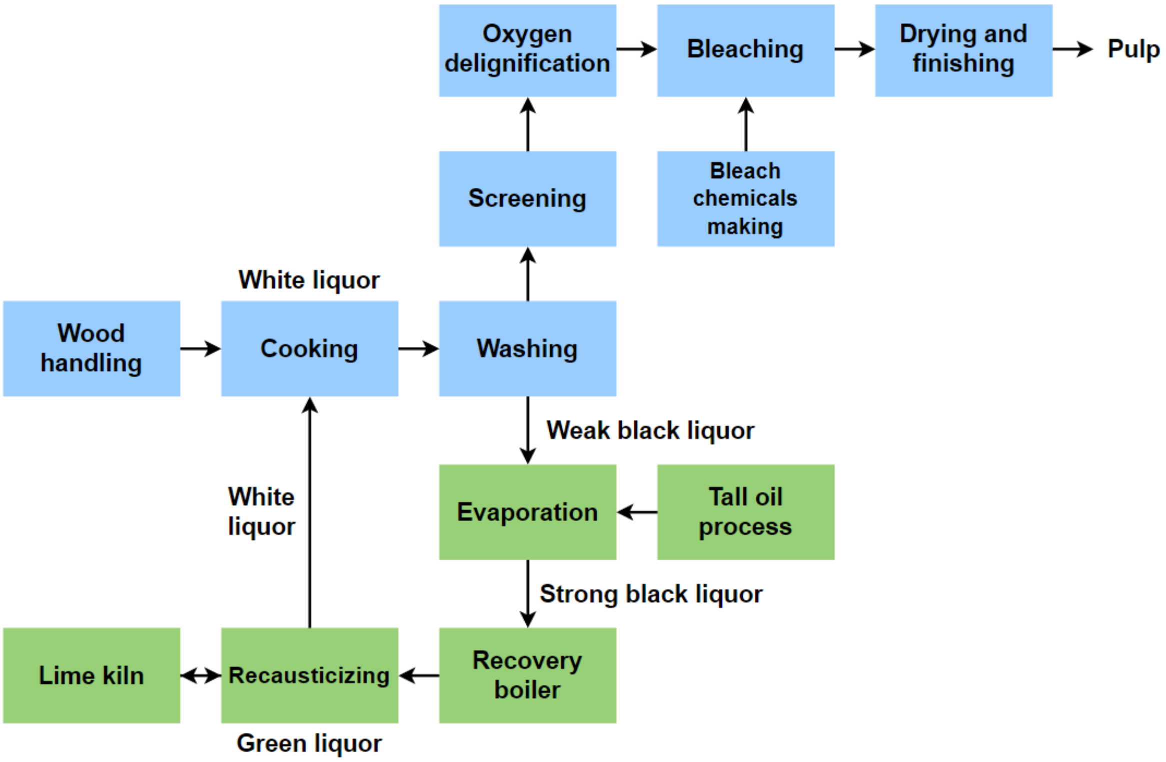


Figure 2. Kraft pulping process flow chart where fiber line is in blue and recovery line in green (KnowPulp n.d.).

In recovery line, the chemicals and energy of Kraft pulp process are recovered, and it includes evaporation, recovery boilers and white liquor preparation. The black liquor formed in the pulp washing goes through evaporation where it is concentrated by removal of water. After evaporation, black liquor is burned in recovery boilers to recover chemicals and energy that can be utilized in the process. The smelt generated in black liquor burning is made into green liquor by dissolving it in water and is then prepared into white liquor that can be returned to the pulping process. White liquor preparation is done by recausticizing and lime reburning in lime kiln. (Suhr et al. 2014, 204-206.)

3.2. Sulfur balance of Kraft pulping

Sodium/sulfur (Na/S) balance is the most important chemical balance of pulp mills (KnowPulp n.d.) as it has effects on the pulping process. Maintaining the Na/S balance is necessary for optimizing the pulp quality, pulping yield and controlling sulfurous emissions of a pulp mill (Mahecha-Botero et al. 2021, 102.) The Na/S balance can be described as sulfidity (KnowPulp n.d.) which is the ratio of Na_2S concentration and active alkali (Gomes & da Silva Junior 2020, 3945). Sulfidity in modern pulp mills is 30-40 % (KnowPulp n.d.) and can be calculated with equation 1 (Bajpai 2018, 334).

$$Sulfidity\ [\%] = \left(\frac{Na_2S}{NaOH+Na_2S}\right) * 100\ \% \tag{1}$$

Sulfur enters and exits Kraft pulping process in several ways. Usual sulfur inputs and outputs of Kraft pulp mill are presented in figure 3 and their typical amounts are shown in table 3. Sulfur comes to the pulping process with wood, water and chemicals (Suhr et al. 2015, 214). Makeup chemicals added to the process to cover sulfur is typically Na_2SO_4 but in modern mills with recovery, they can be replaced by other compounds containing sulfur (Mahecha-Botero et al. 2021, 100). In addition to makeup chemicals, sulfur enters the process via other chemicals: H_2SO_4 in the tall oil production, by-products of chloride dioxide (ClO_2) production and magnesium sulfate ($MgSO_4$) for oxygen delignification. The fuels used in the recovery boiler and lime kiln also bring sulfur to the process. (Suhr et al. 2015, 214; KnowPulp n.d.)

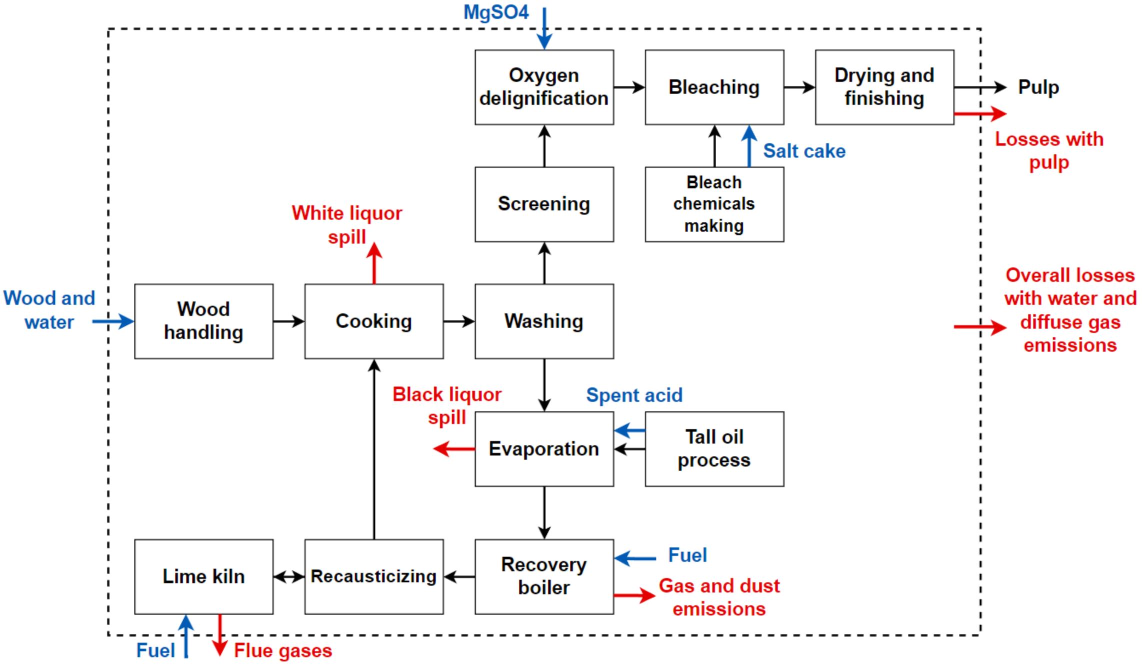


Figure 3. Sulfur inputs and outputs to the Kraft process (Macha-Botero et al. 2021, 101; Valmet 2017, 3; Suhr et al. 2015, 214-215).

Sulfur exits the process through chemical losses. These losses are mainly from brown stock washing, liquor spills, flue gases from recovery boiler and lime kiln (Mahecha-Botero et al. 2021, 100; Suhr et al. 2015, 215) as well as odorous gases (KnowPulp n.d.) which are discussed in more detail in chapter 3.3. Due to improvements in the pulping process the losses in modern Kraft pulp mills are significantly lower than before (Mahecha-Botero et al. 2021, 100). For example, recovery boilers and lime kilns have electrostatic precipitators and flue gas scrubbers that reduce the losses to be insignificant from the sulfur balance perspective (KnowPulp n.d.).

Table 3. Typical amounts of sulfur input and output flows to the Kraft process (Macha-Botero et al. 2021, 101; Valmet 2017, 3; Suhr et al. 2015, 214-215).

Inputs		**Outputs**	
Source	Amount of sulfur [kg S/ADt]	Source	Amount of sulfur [kg S/ADt]
Wood, water, chemicals	0.2-0.5	Pulp and washing loss pulp	0.5-1.5
Fuel to lime kiln and recovery boiler	1-2	Emissions to air	0.2-0.5
Spent acid from tall oil production	2-3	Losses with water effluents	0.5-2
Salt cake from ClO_2 production	3-7	Losses with ash and ash purge	3-5.5
$MgSO_4$ for oxygen delignification	0-0.8	Black liquor and white liquor spills	0.1
Total	6-20	Total	4-10

As the modern pulp mill process includes chemical recovery and closed liquor cycle, the problem is often high sulfidity rather than losses (Valmet 2017, 1-2). High sulfidity impacts the Na/S balance and brings several drawbacks such as increased corrosion problems in the pulp and recovery cycle and negative impacts to the operation of the recovery boiler. Therefore, excess sulfur needs to be managed. (Mahecha-Botero et al. 2021, 102.) There are various methods for dealing with high sulfidity and managing the Na/S balance (Mahecha-Botero et al. 2021, 101) from which commonly is used the purging of by-products from side streams such as neutralized spent acid from chlorine dioxide (ClO_2) production or electrostatic precipitator (ESP) ash from the recovery boiler (Mahecha-Botero et al. 2021, 100; Valmet 2017, 2).

Other methods of controlling sulfidity have also been developed (Mahecha-Botero et al. 2021, 101; Valmet 2017, 4). Reducing the sulfur content can be done by leading totally oxidized white liquor to the bleaching process (Valmet 2017, 4) or by replacing a part of H_2SO_4 with carbon dioxide (CO_2) in tall oil process (Mahecha-Botero et al. 2021, 101). Generator acid purification (GAP) method enables a reduction of bleaching chemicals and makeup chemicals of causticizing process. In GAP, the sodium sesquisulfate ($H_4Na_2O_{12}S_3$) produced in ClO_2 as a by-product is separated into H_2SO_4 and Na_2SO_4. Electrolytic salt splitting can be used to generate sulfur free alkali and H_2SO_4 from ESP salt from the recovery boiler. In ClO_2 production sulfur content can be managed with reduction in the saltcake generation. This can be done by bringing into use improved technologies. For example, bleaching with a mixture of ozone (O_3), oxygen (O_2), hydrogen peroxide (H_2O_2) and ClO_2 reduces the saltcake production. (Mahecha-Botero et al. 2021, 101.)

In addition to the pulp mill sulfidity controlling methods mentioned above, an efficient way of separating the streams of sodium and sulfur exists (Valmet 2017, 2). Managing Na/S balance could be done by internal H_2SO_4 production. By manufacturing H_2SO_4 in the pulp mill, the ability to use excess sulfur and manage Na/S balance could be improved. (Mahecha-Botero et al. 2021, 102.) The production of H_2SO_4 from odorous gases is presented in chapter 3.3 and further discussed in chapter 4.

3.3. Non-Condensable Gases

Odorous components created by pulp mills are called non-condensable gases (NCG) (Hovikorpi & Vakkilainen 2019, 297) that are collected from multiple stages of the pulping process (Mahecha-Botero et al. 2021, 102). NCG contain sulfur as total reduced sulfur (TRS) and are formed in the chemical reactions of Kraft pulping process where chemicals and wood react to delignify and release fibers. Main compounds of NCG are hydrogen sulfide (H_2S), dimethyl sulfide ($(CH_3)_2S$), dimethyl disulfide ($(CH_3)_2S_2$) and methyl mercaptan (CH_3SH). (Hovikorpi & Vakkilainen 2019, 297.) Typically 2-7 kg/ADt of sulfur is contained in NCG in pulp mills nowadays (Mahecha-Botero et al. 2021, 103; Valmet 2017, 5). Kraft pulping creates two types of NCG: concentrated and dilute ones (Hovikorpi & Vakkilainen 2019, 297).

Concentrated non-condensable gases (CNCG) have a high concentration and are able to burn for short time periods. Their concentrations are above the upper explosion level. The main sources of CNCG are the cooking, evaporation, and foul condensate stripper. The CNCG from stripper are called stripper off-gases (SOG) and are one of the largest CNCG streams. Their main component is methanol. Diluted non-condensable gases (DNCG) are weak gases with significantly lower concentration than CNCG. Their concentration should be kept below the lower explosion level. DNCG have various sources in the fiber line, such as screening and washing, as well as evaporation, tall oil cooking and causticizing plant in the recovery line. (Hovikorpi & Vakkilainen 2019, 297-298.) Table 4 presents the possible NCG sources in the fiber and recovery lines. The sources may vary based on how old the mill is (Hovikorpi & Vakkilainen 2019, 301).

Table 4. NCG sources in the fiber line and recovery line (Hovikorpi & Vakkilainen 2019, 298-303).

	CNCG	**DNCG**
Fiber line	Digester	Chip bin Blow, filtrate and reject tanks Brown stock, knot and reject washers MC and vacuum pumps
Recovery line	Evaporation plant Vents from condensate and stripper feed tanks Foul condensate stripper Methanol tank (if mill has methanol liquefaction plant)	Evaporation plant Tall oil plant vents Recausticizing plant Recovery boiler

Pulp mills with a modern design are intended to be free of odorous gas emissions as NCG are collected (Hovikorpi &Vakkilainen 2019, 298). With right design, collection and destruction systems can eliminate more than 99 % of the sulfuric gas emissions (Suhr et al.

2015, 287). CNCG and DNCG are collected separately due to the differences in their explosiveness levels. If they were collected together, they would form an explosive mix. CNCG collection is done using a closed pipeline system with no air leakage. Steam ejectors or water ring vacuum pumps are used for transferring the gases. SOG need to be handled in a separate system from other CNCG. DNCG are collected with ducts where the gases are moved with blowers. In DNCG collection, as much as possible gases are collected and excess air avoided. Overpressure, underpressure, temperature changes and condensation need to be considered in the collection system equipment as they can lead to failures. (Hovikorpi & Vakkilainen 2019, 297-304.)

The usual NCG destruction method is thermal oxidation which can be done by burning the NCG and producing SO_2 (Mahecha-Botero et al. 2021, 102; Suhr et al. 2015, 244). The options for burning NCG are combustion in the recovery boiler, lime kiln and NCG burners (Suhr et al. 2015, 244 & 287) from which the recovery boiler is the most commonly used burner (Hovikorpi & Vakkilainen 2019, 304). When a dedicated NCG burner is used, a scrubber is needed to control the forming SO_2 emissions. Both CNCG and DNCG can be burned in the recovery boiler, CNCG as secondary air and DNCG as secondary or tertiary air. Lime kiln can also be used for both NCG types but DNCG are commonly incinerated in the recovery boiler. (Suhr et al. 2015, 244, 296-297.) SOG are handled with methanol liquefaction after which the NCG are led separately to the CNCG collection system. In older systems, SOG are treated in the NCG burner. (Hovikorpi & Vakkilainen 2019, 300.) In case of a failure, disturbance, and maintenance, mills need to have a backup system for destruction of CNCG. For DNCG a backup system is often not needed (Suhr et al. 2015, 291-292). When recovery boiler is used as a main incinerator, lime kiln, power boiler, dedicated NCG boiler or torch can act as a spare burning place (Hovikorpi &Vakkilainen 2019, 299-300; Suhr et al. 2015, 294-296).

Although thermal oxidation is the most used method of NCG elimination, other methods can also be used. Absorption is another general option, and it is done using scrubbing technologies. These technologies include a spray tower and a packed column. Absorption is mainly used for the destruction of H_2S and CH_3SH. (Suhr et al. 2015, 244.) Another way of handling

NCG is sulfuric acid production from CNCG. The SO_2 produced in the burning of CNCG can be used for the manufacturing of H_2SO_4 (Mahecha-Botero et al. 2021, 102.) This way the sulfur in NCG can be recovered and utilized as sulfuric acid in the process leading to reducing the addition of external sulfur (Valmet 2017, 2). More information about the production of H_2SO_4 in pulp mill is presented in chapter 4.

4. Sulfuric acid production

Sulfur is produced almost solely as a by-product H_2S or other sulfuric compounds from different industries (Wagenfeld et al. 2019, 79). The three biggest sulfur sources for the production of sulfuric acid are elemental sulfur from natural gas purification and petroleum refining, SO_2 from metallurgical refining, and SO_2 from regeneration of spent sulfuric acid that is used as a catalyst (King et al. 2013, 13). This chapter presents different ways of producing sulfuric acid. First is presented sulfuric acid production in Kraft pulping and after that the alternative methods including elemental sulfur burning and utilizing industrial side-streams. Environmental impacts of the production alternatives are also discussed.

There are three ways of producing sulfuric acid: contact process, Topsoe WSA and Sulfacid. The contact process is the most commonly used method, and its main steps are catalytic oxidation of SO_2 to convert it to SO_3 and absorption of SO_3 to form H_2SO_4. The reactions are presented in equations 2 and 3. (Schlesinger et al. 2011, 208-216.) Based on the sulfur component at input, the steps before catalytic oxidation and adsorption can vary (ANDRITZ GROUP 2022b, 4; King et al. 2013, 19; Schlesinger et al. 2011, 208). They are described later in this chapter.

$$SO_2 + 0.5O_2 \rightarrow SO_3 \tag{2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{3}$$

Absorbing SO_3 directly into water is not feasible (Schlesinger et al. 2011, 216) as it produces highly corrosive mist (Benvenuto 2015, 4-5) that can’t be merged together (Schlesinger et al. 2011, 217). Due to that, two additional steps are performed. SO_3 is first absorbed into sulfuric acid which forms oleum ($H_2S_2O_7$) and by adding water to it, sulfuric acid is formed. Equations 4 and 5 show the reactions (Benvenuto 2015, 4-5, Schlesinger et al. 2011, 217.)

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7 \tag{4}$$

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4 \tag{5}$$

The conventional contact process, or single contact process, can be made more efficient by adding another acidmaking stage. In this double contact process, the SO_2 remaining in the exit gases from sulfuric acid making is converted to SO_3 and SO_3 then to H_2SO_4. To enable double contact process, the plant needs to have several catalyst beds. Most industrial sulfuric acid plants have four catalyst beds from which three are typically for the initial acid making and one for the remaining SO_2 gases. In addition to the improvement in sulfuric acid production efficiency, double contact process also reduces the SO_2 emissions. (King et al. 2013, 211 & 222.)

The less used methods of producing sulfuric acid are Topsoe Wet-gas Sulfuric Acid (WSA) process and Sulfacid process. Topsoe WSA includes the same reaction steps as the contact process but the SO_2 oxidation happens in a wet gas. The sulfuric acid forming in the absorption of SO_3 is condensed as it is formed in a gaseous form. Sulfacid process differs from the contact process and WSA process in a way that the transforming of SO_2 to H_2SO_4 happens in one reaction with O_2 and water instead of first forming SO_3. The reaction of the process is presented in equation 6. (Schlesinger et al. 2011, 227-229.)

$$SO_2 + 0.5O_2 + nH_2O \rightarrow H_2SO_4 + (n-1)H_2O \tag{6}$$

As the reaction of forming sulfuric acid from SO_3 is exothermic, releasing thermal energy, the output sulfuric acid needs to be cooled. The energy released in the reaction can be recovered as steam that can be used for example, for generating electricity. For plants that recover the heat as steam, the useful heat recovery rate is more than 90 %. To produce steam in the process, the acid going in the boiler should be as hot as possible while taking into account corrosion which increases when temperature increases. (King et al. 2013, 267-280.)

4.1. Sulfuric acid production in pulp mill

A WSA process can be used to produce sulfuric acid from the odorous gases of pulp mills. In addition to the odorous CNCG, the process can have another sulfur input: molten sulfur as seen in figure 4 presenting the process. (ANDRITZ GROUP 2022b, 4.) The use of supplemental molten sulfur in a WSA process is optional (Mahecha-Botero et al. 2021, 103). If elemental sulfur is used as an additional sulfur input, the sulfur needs to be melted and filtered before the actual process of manufacturing sulfuric acid (King et al. 2013, 21). The filtration is done in order to remove any dust and dirt particles from the sulfur. The sulfur filter is precoated with a filter aid before the filtration and a filter cake is produced in the process. (Sulphuric Acid on the Web 2006.)

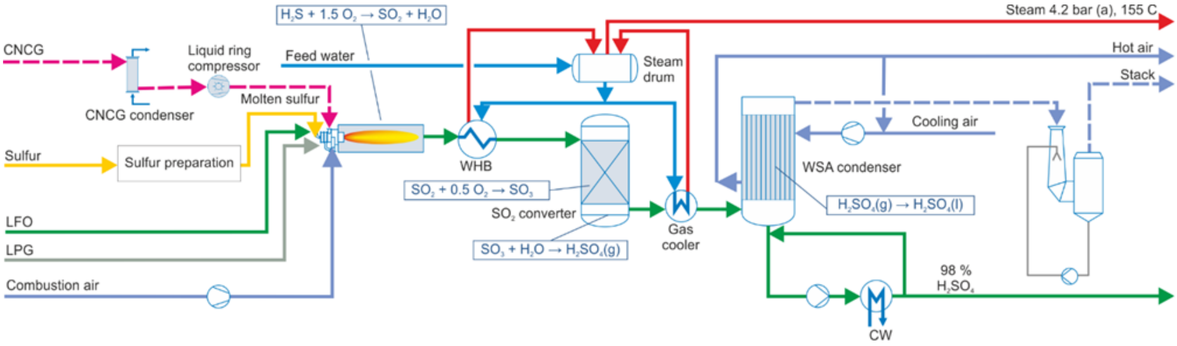


Figure 4. Wet-gas Sulfuric Acid (WSA) process (ANDRITZ GROUP 2022a, 4).

As the WSA process uses wet feed gas, the input gas doesn't need drying pre-treatment (King et al. 2013, 283) and so the first step after the optional melting and filtration phase is the combustion of sulfur inputs including H_2S contained in the CNCG feed gas. The combustion reaction is presented in equation 7. (ANDRITZ GROUP 2022b, 4.) Other sulfur containing compounds of CNCG also burn and form SO_2, H_2O and CO_2 (Mahecha-Botero et al. 2021, 103). The gas is cooled after the incineration in a waste heat boiler where steam is generated. The steam is fed into a steam drum and can be used for cooling the process. (ANDRITZ GROUP 2022b, 4.) The excess steam can be utilized as energy. (Mahecha-Botero et al. 2021, 103.)

$$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O \qquad (7)$$

The next steps are the catalytic oxidation of SO_2 to SO_3 which is done either two or three catalyst beds and the hydration of SO_3 where H_2SO_4 is formed after cooling. The hydration happens in a temperature of about 290 °C. Differing from the contact process, in a WSA process the sulfuric acid product needs to be condensed as a final step. (Schlesinger et al. 2011, 227-228.) A WSA process in a Kraft pulp mill produces sulfuric acid with a concentration of over 95 % (ANDRITZ GROUP 2022b, 4). The exit gases not included in the product are H_2O, O_2, N_2 and CO_2 (King et al. 2013, 286). After cleaning these exit gases can be omitted to atmosphere through a stack (Mahecha-Botero et al. 2021, 103).

Sulfuric acid production from excess sulfur at pulp mill has some advantages for the pulping process. It is a way to control sulfidity without losing the needed sodium (Valmet 2017, 2). As mentioned in chapter 3.2., ash dumping is used as a controlling method for sulfidity. With ash dumping, not only sulfur but also sodium is lost which leads to a need of makeup chemical NaOH (Knowpulp n.d.). Sulfuric acid production reduces the need for recovery ash boiler dumping and the sodium makeup chemical NaOH (Mahecha-Botero et al. 2021, 102). Ash is one of the main solid wastes produced in the pulping process and have typically been disposed to landfills (Hu et al. 2020, 1). With sulfuric acid production, the production of solid waste ash and the impacts of landfilling could be reduced.

Other effects and advantages of producing sulfuric acid from the sulfur containing CNCG have been discussed by Mahecha-Botero et al. (2021), Valmet (2017) and Hovi (2019). Sulfuric acid production would make it possible to simultaneously manage the sulfur balance and handle NCG (Mahecha-Botero et al. 2021, 100-102) as the sulfur containing odorous gases can be fed to the sulfuric acid manufacturing plant at the mill (Valmet 2017, 3-5). The produced sulfuric acid can be used at the pulp mill or sold to other companies (Mahecha-Botero et al. 2021, 102). Internally at the pulp mill, sulfuric acid is used in making valuable products, like tall oil or ClO_2 of side streams by primary acidification (Valmet 2017, 3). If sold, the sulfuric acid could bring revenue. Other advantages of manufacturing sulfuric acid from NCG include savings from the reduction of makeup chemicals needed to maintain the sulfur balance and revenue from steam that can be used for power generation. (Mahecha-Botero et al. 2021, 102.) Production of sulfuric acid also reduces the amount of sulfate effluent that needs to be treated (Valmet 2016).

4.2. Elemental sulfur burning

About 60 % of sulfuric acid manufacture happens from elemental sulfur which is received as a by-product from natural gas and petroleum refining (King et al. 2013, 13). Before the 1980s, elemental sulfur was mined using the Frasch process (Maslin et al. 2022, 2) where superheated water and air are blown to concentric tubes to get sulfur-water mixture out of underground reservoirs (Benvenuto 2015, 3). The Frasch method causes sulfur contamination and acidification of soils of the mining locations (Likus-Cieslik et al. 2017, 2). The process also has a high thermal energy demand and produces big amounts of sulfurous wastewater. Nowadays, the Frasch process is not used as sulfur is extracted from oil and gas refining but due to the decarbonization of the energy system, oil and gas production in decreasing and in the future sulfur by-product might not be as available as today (Maslin et al. 2022, 1-2).

The by-product sulfur is used to desulfurize the oil and gas refining industry as the sulfur emissions from combustion are reduced by utilizing them (Maslin et al. 2022, 1-2). The recovery of elemental sulfur is done by processing H_2S thermally in sulfur recovery units (Abumounshar et al. 2021, 2441). Sulfur recovery from natural gas is shown in equation 8 (Benvenuto 2015, 4).

$$O_2 + 2H_2S \rightarrow 2S + 2H_2O \tag{8}$$

The sulfur burning plants are typically located near the places where sulfuric acid is used. This means the by-product sulfur from petroleum and natural gas refineries needs to be transported to the plant. Elemental sulfur which is produced and combusted molten is also usually transported molten. The transportation of molten sulfur is done via railways in tank cars or sea in barges or ships. Tanker trucks can be used for shorter distances. Sulfur can also be transported as solid pellets or flakes but in those cases, they have to be melted and dirt contained in them filtered out before burning. (King et al. 2013, 20-21.)

The sulfuric acid production from elemental sulfur is done with the contact process and the first step of the process is sulfur burning which is shown in equation 9. Before the actual burning, molten sulfur is atomized from liquid form to gaseous form. After that the burning is done with dried air in a furnace. (King et al. 2013, 19-22.) The product gas from the sulfur burning step contains SO_2, O_2 and nitrogen N_2 at a temperature of about 1150 °C (King et al. 2013, 23). The gas is cooled to about 420 °C and by catalytic oxidation SO_3 is produced from SO_2 (King et al. 2013, 24) The catalyst used in the oxidation is vanadium pentoxide (V_2O_5) (Abumounshar et al. 2021, 2442; Benvenuto 2015, 4). After the catalytic oxidation converter, H_2SO_4 is produced (King et al. 2013, 24).

$$S + O_2 \rightarrow SO_2 \tag{9}$$

Marwa et al. (2017) conducted an LCA study of a Tunisian sulfuric acid production plant where sulfuric acid is produced from elemental sulfur that is first melted and filtered. The study included five subsystems: the production process, the steam and electricity production, transportation of materials, chemical consumables, and equipment. The functional unit of the study was 1 ton of produced sulfuric acid, so the environmental impacts were presented according to it. The study used three impact assessment methods: the ILCD 2011 Midpoint + V1.09, the CED, and the CExD method. Total of sixteen impact categories were assessed and five of them were considered relevant for sulfuric acid production. Those were climate change, acidification, eutrophication, ozone depletion and photochemical ozone formation. (Marwa et al. 2017, 259-264.) From those, ozone depletion and photochemical ozone formation are not presented here as they are not part of the selected impact categories in this thesis. Global warming potential (GWP) of the sulfuric acid production was 88.92 kg CO_2 eq/t. Acidification potential (AP) was 4.01 mol H+ eq/t. Eutrophication potential (EP) was presented as terrestrial EP, marine EP and freshwater EP. The results were 1.79 mol N eq/t for terrestrial EP, 166.77 g N eq/t for marine EP and 12.27 g P eq/t for freshwater EP. (Marwa et al. 2017, 264-265.)

Another LCA study done on sulfuric acid production from elemental sulfur was conducted by Adeniran et al. (2017) on a Nigerian sulfuric acid plant. The study took into account the sulfuric acid production with raw material extraction but exclude equipment and transportation. The functional unit used in this study was 1 kg of produced sulfuric acid and was scaled to 50 000 tons. CML 2001 – Nov 2010 was the used impact assessment method. Ten environmental impact categories were selected, and the study did not bring up any of the impact categories as more relevant than others. From the impact categories, GWP, AP, EP, human toxicity potential (HTP), water depletion potential (WDP) and abiotic resource depletion potential (ADP) are presented here as they are selected for the impact categories in this thesis. (Adeniran et al. 2017, 3-13.) They are calculated to present 1 ton of produced sulfuric acid to improve the comparability to other studies presented in this thesis. GWP of the plant was 270 kg CO_2 eq/t, AP 4.36 kg SO_2 eq/t, EP 0.138 kg Phosphate eq/t, and HTP 15.8 kg 1,4-DB eq/t (Adeniran et al. 2017, 13).

4.3. Metal sulfide roasting and smelting off-gases

A large amount of sulfuric acid is manufactured as a by-product in metal refining industry (Jantunen et al. 2019, 101). In fact, about 30 % of all sulfuric acid is produced from the off-gases from smelters and roasters in metal sulfide processes (King et al. 2013, 31). The off-gases containing SO_2 needs to be captured and handled. The production of sulfuric acid from the SO_2 is a typical way of handling it in metallurgical plants. (Schlesinger et al. 2011, 206.) In addition to functioning as a SO_2 handling method, sulfuric acid production is beneficial for metal refining industry as it creates a useful sulfuric acid product (King et al. 2013, 31). A disadvantage is that the SO_2 gas needs to be immediately converted to sulfuric acid and storing and transporting it is more dangerous and costly than elemental sulfur. Some sulfide minerals also have toxic heavy metals in them that can cause contamination. (Maslin et al. 2022, 2-4.)

Metal sulfides can be divided into pyrite, also called iron sulfide (FeS_2) (Runkel & Sturm 2009, 101) and other metal sulfides such as copper (CuS), zinc (ZnS) and lead sulfides (PbS) (Fertilizers Europe 2000, 22-24). Thus, pyrite roasting can also be classified into its own category of sulfuric acid production (Runkel & Sturm 2009, 101-102; Fertilizers Europe 2000, 22) Copper smelting process reaction is presented as an example in equation 10 (Amiri & Alihosseinpour 2015, 88).

$$CuFeS_2 + O_2 \rightarrow CuFeS + FeO + SO_2 \tag{10}$$

Physically metallurgical sulfuric acid manufacturing process is the most complex out of the sulfuric acid plant types (Amiri & Alihosseinpour 2015, 88). The production can be done using any of the three process types: contact process, WSA or sulfacid. With contact process, the production steps are the same as described in chapter 4. (Schlesinger et al. 2011, 208.) As the off-gases are in the form of SO_2, there does not need to be a conversion before the oxidation and absorption but other pre-treatment is required. The gases need to be cooled, cleaned and dried (King et al. 2013, 31). The process is shown in figure 5.

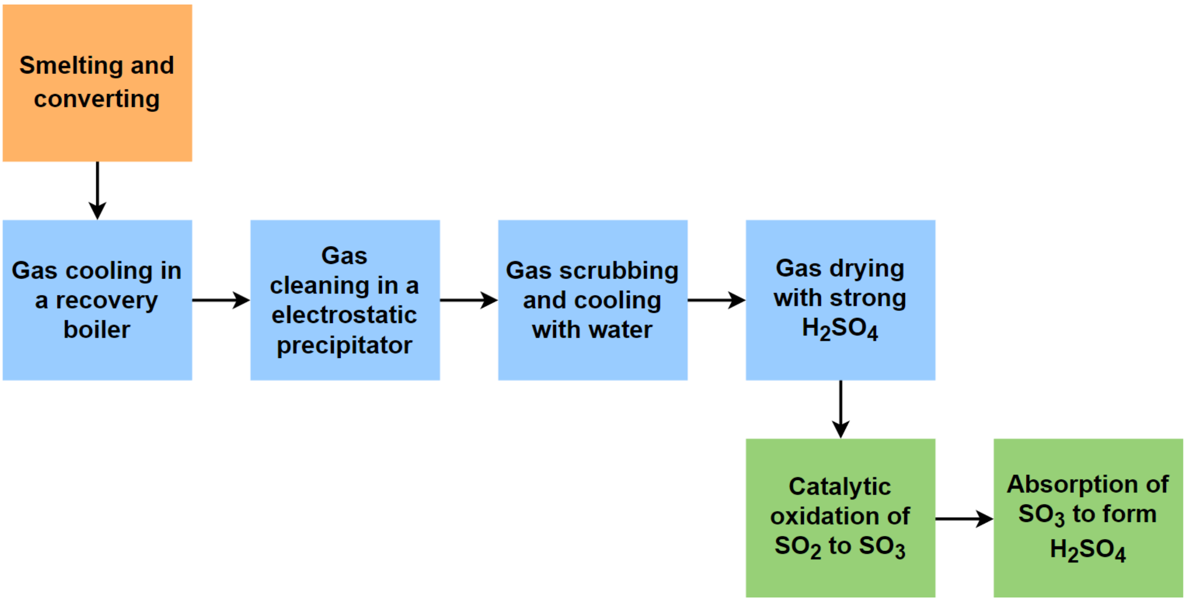


Figure 5. Sulfuric acid production process from smelter and converter off-gases (King et al. 2013, 31-33; Schlesinger et al. 2011, 209).

First, the off-gases need to be cooled which is done in a heat recovery boiler so the heat can be recovered as steam. The cooling is a preparation step for the electrostatic precipitator where the gas is then cleaned. The electrostatic precipitator removes dust contained in the gas. (King et al. 2013, 34-35.) After that, the gas is scrubbed and cooled by adding water. This step removes any remaining impurities. As the final step before the off-gas is ready for the acidmaking steps is the drying which is done in a drying tower. The gas is contacted with strong sulfuric acid which removes the H_2O in the gas. (Schlesinger et al. 2011, 211-212.) The gas then goes through the sulfuric acid production phases after which the product is stored and transported to consumers (Kekkonen et al. 2013, 8). In metallurgical sulfuric acid production, the end-product sulfuric acid is transported to the point-of-use rather than the raw material sulfur to the point-of-production. This is because the production happens as a by-production. (King et al. 2013, 14.) The transportation can be done as a road or rail transport (Kekkonen et al. 2013, 8; King et al. 2013, 14).

An LCA study by McLean et al. (2022) was done on a plant using SO_2 off-gases from metal ore smelting in Ontario, Canada. The study was a comparison of an existing plant and a proposed heat recovery system. The system boundary included the sulfuric acid plant and 1 kt of produced sulfuric acid was used as the functional unit. The selected impact categories of the study were GWP, AP, EP and relative human toxicity potential HTP and they were assessed using TRACI. These four impact categories were considered to represent the environmental impact of the sulfuric acid production. (McLean et al. 2022, 656-660.) The results of this study were calculated to correspond to 1 ton of sulfuric acid. GWP of the study was 1.46 kg CO_2 eq/t, AP 0.034 kg SO_2 eq/t, EP $1.71 \cdot 10^{-3}$ kg N eq/t and HTP $2.33 \cdot 10^{-7}$ CTUh/t (McLean et al. 2022, 661). However, because the system boundary only included the sulfuric acid plant and not the production of energy other than electricity or materials needed in the process, the study is not comparable to the study conducted in this thesis.

4.4. Regeneration of spent sulfuric acid

About 10 % of the SO_2 used in the production of sulfuric acid is obtained from regeneration of spent sulfuric acid which is used as a catalyst for alkylation. Sulfuric acid is used as a catalyst in various industrial process, like the production of petroleum products and polymers. A catalyst is not consumed in a process where it is used so the volume of sulfuric acid does not decrease. There are, however, impacts on the effectiveness, also called activity, of the acid. (King et al. 2013, 47.) With time, the activity is reduced (Wahoud et al. 2011, 31) because of contamination with water and chemicals such as hydrocarbons used in the processes (King et al. 2013, 47). Two examples of spent alkylation catalysts and the contaminants they contain can be seen in table 5.

Table 5. Compositions of two spent alkylation catalysts (King et al. 2013, 49).

Component (mass %)	**Spent catalyst from petroleum alkylation catalysis**	**Spent catalyst from methyl methacrylate catalysis**
H_2SO_4	90	15
H_2O	3-5	25
Dissolved hydrocarbons	4-7	5
Ammonium bisulfate	-	45
Acetone disulfonic acid	-	5
Low fuel value tars	-	5
Particulates (mainly iron)	< 100 ppm	-

When the catalyst's activity is reduced enough, the spent catalyst needs to be regenerated so it can be reused. As spent catalysts are hazardous (Wahoud et al. 2011, 31), highly corrosive and possibly reactive even in storage and transportation (King et al. 2013, 51), the regeneration of them is important (Wahoud et al. 2011, 31). The aim of the regeneration process is to return the spent acid to a strong acid which is done with a process containing several steps.

First, the spent acid is handled by decomposing the sulfuric components in a furnace. (King et al. 2013, 47-51.) The decomposition reaction (King et al. 2013, 51) is following:

$$H_2SO_4 \rightarrow SO_2 + 0.5O_2 + H_2O \tag{11}$$

The next steps of the regeneration process are the same as in the previously introduced sulfuric acid production processes: The produced SO_2 is oxidized into SO_3 and then H_2SO_4 is produced from SO_3. If the regeneration happens with contact process, the off-gas from the furnace first goes through through cooling, cleaning, condensing and dehydrating steps. In a heat recovery system the off-gas is cooled and then soot and ash are cleaned from it. H_2O in the gas is condensed and removed with strong sulfuric acid. Before the dehydration, air is added to the gas to increase the amount of O_2. (King et al. 2013, 47-56.) The regeneration can also be done with the WSA process (Atanasova 2017, 58; Laursen & Karavanov 2006, 229), in which case drying and scrubbing of the wet gas are not needed (Laursen & Karavanov 2006, 230-232).

4.5. Sulfate roasting

Another way of manufacturing sulfuric acid is the decomposition of sulfates into SO_2 (Fertilizers Europe 2000, 25). Sulfates used for the sulfuric acid production are mainly iron sulfate ($FeSO_4$) and calcium sulfate ($CaSO_4$) but also others such as manganese sulfate ($MnSO_4$) (Hammerschmidt & Wrobel 2009, 87). Iron sulfate is a waste stream from for example, the pigment industry (Hammerschmidt & Wrobel 2009, 87). Calcium sulfate is the major component of gypsum which is an industrial by-product and produced in large amounts as waste from which only a small portion is recycled (Wu et al. 2020, 1). Decomposing calcium sulfate is a way of treating waste gypsum with also producing useful sulfuric acid as a product. (Hammerschmidt & Wrobel 2009, 87).

The decomposition of sulfates is done by roasting the sulfate in a fluid-bed furnace, a multiple-hearth furnace or a rotary kiln. After the decomposition, the SO_2 gas goes through cooling and cleaning before entering the acidmaking process. (Fertilizers Europe 2000, 25-26.) The decomposition of iron sulfate is shown below as an example of sulfate decomposition reaction. The reaction can either be done in one step as seen in equation 12 or in two steps like in equations 13 and 14. (Hammerschmidt & Wrobel 2009, 95.)

$$2FeSO_4 \rightarrow 2FeO + 2SO_2 + O_2 \tag{12}$$

$$FeSO_4 \rightarrow FeO + SO_3 \tag{13}$$

$$SO_3 \rightarrow SO_2 + 0.5O_2 \tag{14}$$

The calcium sulfate of gypsum can also be used for the co-production of calcium sulfoaluminate clinker and sulfuric acid. production of calcium sulfoaluminate generates SO_2 which can be transformed into sulfuric acid. (Wu et al. 2020, 1.) The equations 2 and 3 from chapter 4 are the acidmaking steps (Justia 2010).

5. Life Cycle Assessment

This chapter focuses on the empirical part of the study, the life cycle assessment. To assess the environmental impacts of sulfuric acid production, LCA methodology is used and ISO standards 14040 and 14044 concerning LCA studies applied. LCA studies. According to the ISO 14040 (2006, 7-16) and 14044 (2006, 7-23), LCA study consists of four phases: goal and scope definition where the objectives and boundaries of the study are defined, life cycle impact inventory that includes data collection and calculation, life cycle impact assessment presenting the environmental impacts and life cycle interpretation where the results of the study are interpreted.

5.1. Goal and scope

The goal of the LCA study is to find out the environmental impacts of the sulfuric acid manufacturing process at a Kraft pulp mill on selected impact categories. They are global warming potential, acidification potential, eutrophication potential, water depletion potential, abiotic resource depletion potential and human toxicity potential. The environmental impacts are compared to the environmental impacts of alternative production methods of sulfuric acid. The study is done for ANDRITZ, and the intended audience of the study are the customers of ANDRITZ. The LCA is conducted as a part of a master’s thesis and disclosed to the public. The study is reported according to ISO standards 14040 and 14044. The LCA modelling is done using GaBi Solutions software by Sphera.

The product system studied in this LCA study is a sulfuric acid manufacturing process at a non-integrated softwood Kraft pulp mill, more specifically a WSA process in a plant located in Finland. The product system produces sulfuric acid with concentration of over 95 % from odorous gases from the pulping process. Two versions of the product system are modelled: one with elemental sulfur as additional sulfur input and one without it. For both versions of the process, the functional unit is 1 ton of produced sulfuric acid. The functional unit is the reference unit for the study and the flows are quantified based on it.

The system boundary of this study includes the production phase of the life cycle as well as the production of needed materials and energy. Transportation of the materials and wastes is also taken into account. The distribution, use and end-of-life parts of the life cycle are excluded from the study. In the process with elemental sulfur, sulfur preparation including melting and filtration is included in the system boundary. The sulfuric acid production itself includes the WSA production steps introduced in chapter 4.1. The system boundaries of each process versions are presented in figures 6 and 7. GaBi models of both processes are shown in appendices 1 and 2.

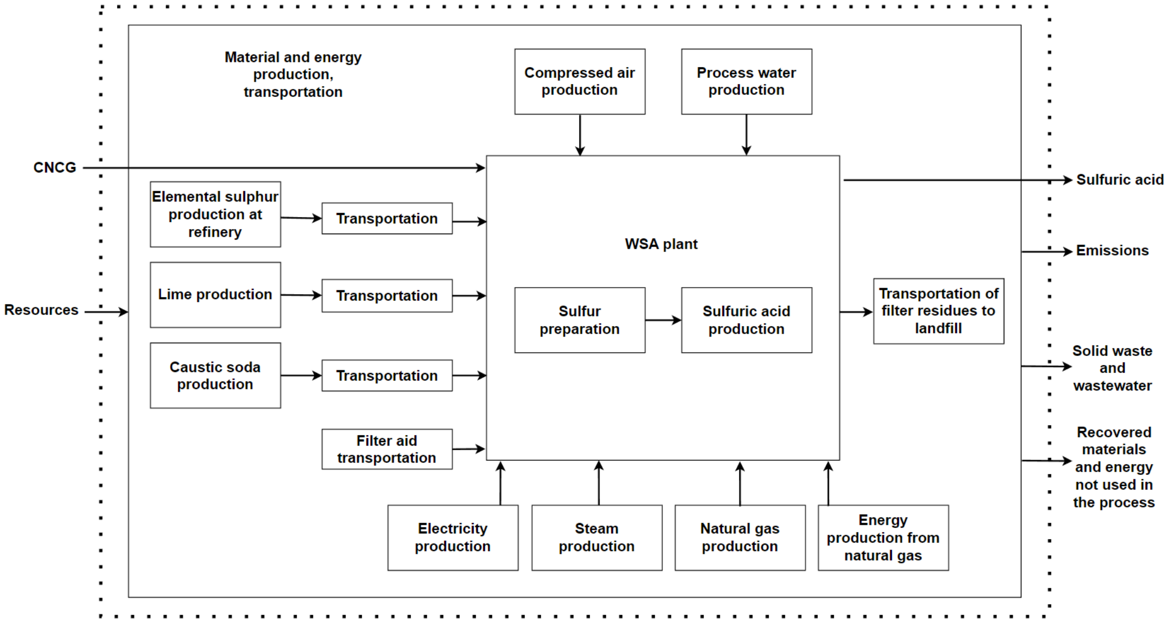


Figure 6. System boundary of the product system with elemental sulfur.

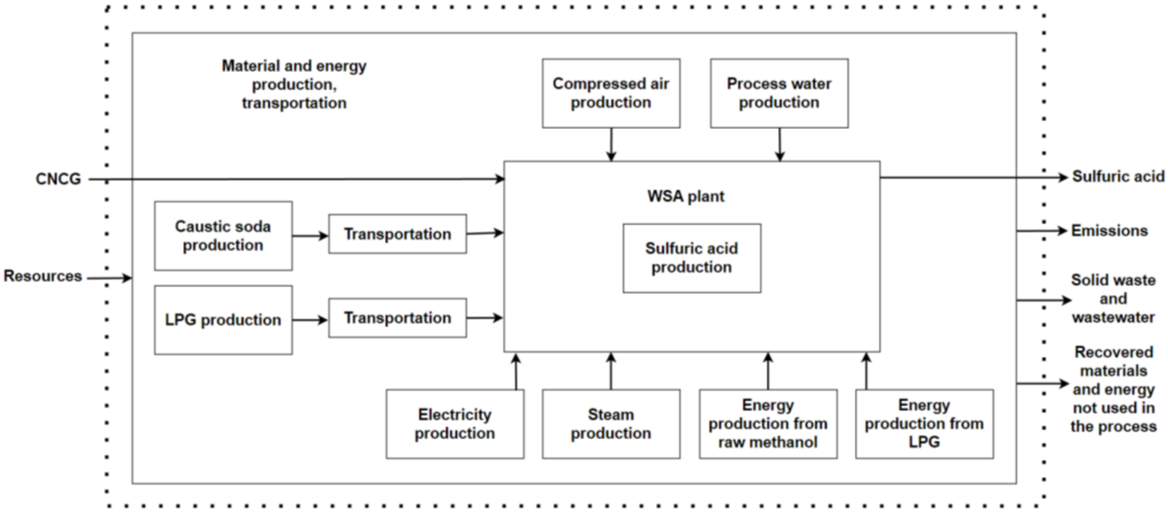


Figure 7. System boundary of the product system without elemental sulfur.

Flows left out of the study are firefighting water, potable water, sealing water, cooling water, chilled water for heating, ventilation and air conditioning (HVAC), CNCG, flue gases, excess steam, wastewater, air input and hot air output. Firefighting water, potable water and HVAC water are excluded because they are not directly for the actual process. Sealing water and cooling water are in closed cycles and their processing is assumed not to have significant impact. CNCG can be classified as a side stream from the pulp mill (Pöyry 2018, 28), thus their production is not part of the environmental impact of the sulfuric acid production. Flue gases are cleaned and released to the atmosphere thus they are excluded from the study. Similarly, the assumption of non-significant impact is made to non-processed air and hot air. Excess steam is assumed to be used in other pulp mill processes and thus left out of the study. Wastewater is not taken into account because wastewater treatment is not included in the system boundary.

5.2. Life Cycle Inventory Analysis

This chapter presents the LCI part of the study where the collection and calculation of data is reported. It includes checking the validity of the collected data and relating it to the functional unit by calculation procedures. The data collection included receiving data from ANDRITZ and searching for information from the GaBi database and literature.

5.2.1 Data collection

The primary data used in the study was WSA process balances from ANDRITZ. These balances were based on sizing data from equipment manufacturer from the year 2022 and contained the input and output flow values of a sulfuric acid production process at a Kraft pulp mill. Secondary data complementing the primary data was gathered from GaBi and literature. The database used in GaBi was Professional and Extended database version 2020.1. Complete processes from the GaBi database were used for the unit processes in the model. The data from GaBi was selected to represent Finland or European Union when the selection was possible to make. The processes used for modelling are presented in appendices 3 and 4. Additional values needed for calculations were obtained from literature sources. These sources were from after the year 2020 and are presented in chapter 5.2.2 table 8.

For the process with elemental sulfur, some assumptions were necessary for the sulfur preparation. The elemental sulfur is assumed to be a side stream from a refinery. The lime used in the pre-treatment of elemental sulfur is slaked lime ($Ca(OH)_2$). Another material used in the process is caustic soda for sulfur handling scrubber in the concentration of 100 % and 20 %. For modelling purposes, it is assumed that the 100 % caustic soda is diluted to 20 %. The water used for the dilution is assumed not to have significant impact, so it is excluded. The caustic soda with the concentration of 20 % used for sulfur handling scrubber is recovered after use. Because of this, it is assumed that they can be returned to the process thus it is only needed in startup. Caustic soda with concentration of 100 % is also used in flue gas scrubber in both versions of the process. This caustic soda is also recovered and returned to the processes.

For both versions of the process, it is assumed that the needed electricity is produced by black liquor combustion in recovery boiler as the plant is located at pulp mill. According to Gomez et al. (2006, 2.19) black liquor is classified as solid biofuel and as there was not available production process in GaBi database for electricity production from black liquor, a process of electricity production from solid biomass is used.

Process waters are assumed to be processed with ion exchange. To simplify the modelling, an assumption is made that both mill water and demineralized water are surface water processed the same way. The production of the process water does not include desalination because the water can be assumed to be fresh water based on the plant's location of Finland. For the compressed air and instrument air, an assumption of 10 bar pressure and high efficiency is made.

In transportation, the materials transported to the plant and the wastes transported to landfill are taken into account. The inputs transported to the plant in the process with elemental sulfur are elemental sulfur, lime, caustic soda, startup sulfuric acid and diatomacea filter aid. In the process without elemental sulfur and caustic soda are transported to the plant. Transportation is assumed to be done with road transport. In modelling, Euro 6 trucks with 20–26-ton gross weight and 17.3 payload capacity are used. They are representative of the Euro vehicle emission standard from 2014 (Williams & Minjares 2016, 8). The transportation distance is estimated based on the production possibilities in Finland. As the estimations gave similar distances for elemental sulfur, lime and caustic soda, the same distance of 250 km is used for all of the inputs. For diatomacea filter aid, there was a lack of information about the transportation distances, but the same assumption was used for it as well. To landfill is transported filter cake that is formed in the filtration of elemental sulfur. It is assumed that landfills are located near the production places thus the distance used for the transportation of filter cake is 10 km. Due to lack of information about the emissions of diatomacea filter aid production and the landfilling of filter cake, they are excluded from the study and only the transportation is included.

The processes produce steam that is assumed to be returned to the process itself. Steam produced from black liquor combustion is thus only needed in startup. Excess steam is also produced, and it could be recovered as energy. However, in this study the recovered energy is not taken into account and assumed that the steam is used in other processes in the pulp mill.

Fuels used in the processes are natural gas for mist control in the process with elemental sulfur and raw methanol as a support fuel in the process without elemental sulfur. Raw methanol is generated as a by-product from the pulping process, so only the combustion is taken into account. Because the raw methanol is biobased, a GaBi process of thermal energy from biomass is used in the modeling. The GaBi process is for solid biomass which is why a bigger value range is considered for raw methanol to take into account the error.

5.2.2 Data reliability

The data is based on sizing data from equipment manufacturer and not on measurements from a plant in operation which is why the study is not specific for an actual operating sulfuric acid plant. The data and assumptions are selected according to the goal and scope of this study and are reliable and appropriate for this purpose. Because of this they might not be suitable for other uses. Thus, the results of this study are not to be used as scientific references but rather suggestions of how and where the environmental impacts of the studied processes are generated. The results are representative of the scope of this study and the assumptions which should be taken into consideration when reviewing them.

5.2.3 Data calculation

For both versions of the process, the primary data was calculated to represent a production of 1 hour and then to correspond to the functional unit of 1 ton of sulfuric acid produced. The primary data was received with value ranges for the inputs and outputs and to take this uncertainty into account, three scenarios of both versions of the process were modelled: baseline scenario with average values, and two other scenarios with minimum and maximum values. It was assumed that the amount of sulfuric acid product is the same in each scenario thus the inputs and outputs were calculated to correspond the same amount of sulfuric acid.

The primary data did not include value ranges for elemental sulfur input nor 20 % caustic soda. An assumption of a variation of +/- 10 % for their values was made. For transportation distances the variation was assumed to be +/- 20 % in both versions of the process. The inputs and outputs of the processes with their uncertainty ranges are presented in tables 6 and 7.

Table 6. Inputs and outputs of the process with elemental sulfur.

Input	**Value range**	**Unit**
Elemental sulfur	145-180	kg
Lime	1.30-1.33	kg
Diatomacea filter air	0.30-0.33	kg
Caustic soda 100 %	2.8-3.6	kg
Compressed air	310-380	Nm^3
Process water	6800-7300	kg
Natural gas	0.3-0.5	kg
Thermal energy from natural gas	13-26	MJ
Electricity	730-900	MJ
Distance to plant	200-300	km
Output	**Value range**	**Unit**
Sulfuric acid product	1000	kg
Distance to landfill	8-12	km

Table 7. Inputs and outputs of the process without elemental sulfur.

Input	**Value range**	**Unit**
Caustic soda 100 %	55-60	kg
Compressed air	140-160	Nm^3
Process water	8200-9400	kg
Thermal energy from raw methanol	1200-1600	MJ
Electricity	990-1030	MJ
Distance to plant	200-300	km
Output	**Value range**	**Unit**
Sulfuric acid product	1000	kg

Some calculations were necessary in order to get the data in right form for modelling. The necessary values of calculations can be seen in table 8 with their sources. The calculations included a dilution calculation of caustic soda with the concentration of 100 % to 20 %, conversion of volumes into masses and calculation of produced energy.

Table 8. Additional values needed in the calculations.

	Value	**Source**
Density of 20 % caustic soda	1180 kg/m^3	LabChem 2020, 4
Heating value of purified methanol	22.7 MJ/kg	Jensen et al. 2012, 2151
Heating value of steam	2.78 MJ/kg	GaBi
Heating value of natural gas	48.7 MJ/kg	GaBi
Heating value of LPG	46.2 MJ/kg	GaBi
Standard volume of natural gas	1.35 Nm^3/kg	GaBi

5.2.4 Sensitivity analysis

The study includes sensitivity analysis where the impact of variables on the results is examined. The sensitivity analysis has two parts: the impact of energy sources and impact of a startup situation compared to a normal operation. The impact of energy sources to the results is examined by changing the electricity production method. In the base situation, electricity is produced with black liquor combustion. In the sensitivity analysis, the replacing source of electricity is Finnish grid mix which is based on the Finnish electricity grid in 2017 thus including both fossil and renewable energy resources.

To examine how a startup of the sulfuric acid plant differs from the normal, continuous production, a startup situation is modelled for both process versions. In startup, some additional inputs are needed which is why considering the startup is important when assessing the environmental impacts. It is assumed that startup happens once a year. The startup is a batch process but because of primary data being in units per hour, an assumption is made that startup lasts for 1 hour. With this assumption the inputs are calculated for the production of 1 ton of sulfuric acid.

The inputs for startup are presented in tables 9 and 10. As these inputs are additional, the flows presented for normal operation remain for startup situations as well. It is assumed that more electricity is not needed in startup compared to normal operation in either of the process versions. Flows that are returned to the process in normal operation need to be produced otherwise for startup. These include steam, 20 % caustic soda for sulfur handling scrubber and 100 % caustic soda for flue gas scrubber. The steam produced for startup is assumed to be from black liquor combustion. Other necessary flows for the process with elemental sulfur are natural gas as fuel and thermal energy from natural gas. For the process without elemental sulfur, LPG is used in startup. The support fuel in startup could also be purified methanol or for example natural gas or bio ethanol. Due to a lack of information available on the environmental impacts of purified methanol, LPG is selected for the startup fuel. The amount of LPG is calculated from the amount of purified methanol and the produced energy which was given in the primary data. The heating values which are used for the calculation can be seen from table 8.

Table 9. Inputs for startup of the process with elemental sulfur.

Startup input	**Value range**	**Unit**
Caustic soda 20 %	3.1-3.8	kg
Caustic soda 100 %	6.6-7.3	kg
Steam	1800-2000	MJ
Natural gas	11-13	kg
Thermal energy from natural gas	550-600	MJ

Table 10. Inputs for startup of the process without elemental sulfur.

Startup input	Value range	Unit
Steam	3900-4500	MJ
Caustic soda 100 %	55-60	kg
LPG	0.25-0.50	kg
Thermal energy from LPG	12-24	MJ

When taking into account both the two electricity production methods and the two situations of operation, four scenarios are created for each version of the process, together eight scenarios. In order to make the reporting simpler, the scenarios are names SC1-SC8 like shown in table 11. Scenarios SC1-SC4 are for the process with elemental sulfur and SC5-SC8 for the process without elemental sulfur. SC1 and SC5 are defined as the baseline scenario for each process.

Table 11. Scenarios of the production process.

Scenario	Process	Operation	Electricity production
SC1	With elemental sulfur	Normal operation	Black liquor
SC2	With elemental sulfur	Normal operation	Grid mix
SC3	With elemental sulfur	Startup	Black liquor
SC4	With elemental sulfur	Startup	Grid mix
SC5	Without elemental sulfur	Normal operation	Black liquor
SC6	Without elemental sulfur	Normal operation	Grid mix
SC7	Without elemental sulfur	Startup	Black liquor
SC8	Without elemental sulfur	Startup	Grid mix

5.3. Life Cycle Impact Assessment

In this chapter, the assessment methods, environmental impact categories and their units are presented. The environmental impacts are studied based on the impact categories selected in the scope of the study. They are global warming potential, acidification potential, eutrophication potential, human toxicity potential, water depletion potential and abiotic resource depletion potential. Global warming potential is used to determine the impact on climate change, and it takes into account greenhouse gases (GHG) (Ecochain 2021). It is selected for this study because climate change is one of the biggest environmental issues currently.

Acidification potential defines the acidifying impact (Ecochain 2021) based on the amount of SO_2 or H+ depending on the assessment method. Eutrophication potential describes the enrichment of nutritional elements. Contributors to EP are N and P emissions and based on the method it can be presented either by the amount of P or N. (Ecochain 2021.) Eutrophication potential can be divided into terrestrial, freshwater and marine potential (Agribalyse 2020). Acidification and eutrophication potentials are selected as impact categories because of the location of the studied sulfuric acid plant. Acidification and eutrophication have been problems in Finland and the studied product system can have emissions affecting them. Only terrestrial and freshwater eutrophication potentials are taken into account because marine eutrophication potential concerns sea water and the Baltic Sea at the west and south coast of Finland is considered brackish water as its salinity is low (MarineFinland 2020).

Water depletion potential assesses the water consumption and depletion (Agribalyse 2020) taking into account the net withdrawal of water (Sphera 2020, 25). As the processes use considerably large amounts of water, water depletion potential, more specifically water scarcity potential is chosen to be in the study. Abiotic resource depletion potential represents the depletion of non-renewables and can assess either fossil energy sources such as oil, coal and gas, or non-renewable minerals and metals (Agribalyse 2020). Abiotic resource depletion potential is selected for this study because the product system uses non-renewable resources. Human toxicity potential indicates the impact of toxic substances on human health. (Ecochain 2021) and it can correspond to either carcinogenic toxicity or non-carcinogenic toxicity. Human toxicity potential is selected as one of the impact categories due to possible human health affecting emissions from pulp mills.

The methodology used in this study is Environmental Footprint 3.0. The Environmental Footprint (EF) is a methodology of environmental performance initiated by European Commission and the version 3.0 is the second version after the pilot phase 2.0 (Sphera n.d.). However, EF 3.0 is not comparable to all the results of the previous studies since they have used different methodology that present the environmental impacts in different units. Thus, multiple methods were used in order to obtain the results in comparable units. The assessment methods that were used in addition to EF 3.0 are CML 2001 – Jan 2016 and ReCiPe 2016 v.1.1 Midpoint (H). In CML 2001 – Jan 2016, GWP, AP and EP are midpoint approaches and HTP is endpoint approach. The other two methods are midpoint approaches. The units of the impact categories of each assessment method are presented in table 12. The human toxicity unit is Comparative Toxicity Unit for human health (CTUh) which represents disease cases per kg of emitted substance (Eckelman 2016, 3259). The water depletion potential unit m^3 world eq equals to the average m^3 of water consumed in the world (Wulca n.d.) and takes into account the availability of water in different locations of the world (Sphera 2020, 25).

Table 12. The units of the impact categories in each assessment method.

	Environmental Footprint 3.0	**CML 2001 – Jan 2016**	**ReCiPe 2016 v.1.1 Midpoint (H)**
GWP	kg CO_2 eq	kg CO_2 eq	kg CO_2 eq
AP	mol H+ eq	kg SO_2 eq	kg SO_2 eq (terrestrial)
EP	-	kg Phosphate eq	-
EP freshwater	kg P eq	-	kg P eq
EP terrestrial	mol N eq	-	-
HTP	CTUh	kg DCB eq	kg 1,4-DB eq
WDP	m^3 world eq	-	m^3
ADP minerals & metals	kg Sb eq	kg Sb eq	kg Cu eq
ADP energy carriers	MJ	MJ	kg oil eq

5.4. Life Cycle Interpretation

In this chapter, the results of the LCA study are presented and interpreted. Table 12 shows the results of SC1 and SC5 because they are the baseline scenarios of each version of the process. As seen from the table, the environmental impacts are lower for the process without elemental sulfur in all impact categories except terrestrial EP and WDP.

Table 13. The results of SC1 and SC5 in EF 3.0.

Impact category	**SC1**	**SC5**
GWP (kg CO_2 eq/t H_2SO_4)	142	25
AP (mol H+ eq/t H_2SO_4)	0.71	0.61
EP freshwater (kg P eq/t H_2SO_4)	$7.0 \cdot 10^{-4}$	$4.7 \cdot 10^{-4}$
EP terrestrial (mol N eq/t H_2SO_4)	1.8	2.2
WDP (world m_3/t H_2SO_4)	310	386
ADP minerals & metals (kg Sb eq/t H_2SO_4)	$2.1 \cdot 10^{-5}$	$5.4 \cdot 10^{-6}$
ADP energy carriers (MJ/t H_2SO_4)	5967	383
HTP cancer (CTUh/t H_2SO_4)	$9.3 \cdot 10^{-8}$	$3.4 \cdot 10^{-8}$
HTP non-cancer (CTUh/t H_2SO_4)	$4.6 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$

The results of the other scenarios with sensitivity analysis are presented in figures in chapters 5.4.1.-5.4.6. The figures show errors resulting from the uncertainty of input and output values. For some of the impact categories, the inputs and outputs have a quite large effect and can lead to notably higher or lower impacts. For the scenarios with higher impact in comparison to the other scenarios, the error is also bigger and leads to more uncertainty toward both lower and higher potential.

The figures also show which flows contribute most to the potentials and it can be seen that there are differences between the impact categories and scenarios. For the process that uses elemental sulfur, the production of elemental sulfur has a big impact in almost every category and could be presented as the main contributor. For the process where elemental sulfur is not used there is not as clear contributor. For both of the process versions, electricity production plays a notable role in most of the categories. In freshwater EP and WDP, the production of process water accounts for most of the potential. In startup, steam production, the additional caustic soda and the use of natural gas as supporting fuel increases the impact in several impact categories. The production of lime, natural gas for mist control, use of LPG and transportation has very small impacts in every category. The contribution of the compressed air and combustion of raw methanol is very dependent on the impact category.

Some of the assumptions made in the scope of this study could affect the results. All of the process water was modeled as demineralized which may result in higher potentials than in reality. Mostly this assumption affects the freshwater EP and WDP where process water is one of the main contributors. Another assumption which might have an impact on the results is that for black liquor, combustion process of solid biomass was used. Solid biomass has higher efficiencies in combustion than liquid biomass. With lower efficiency, the environmental impacts caused by the combustion of black liquor could in reality be higher than the results. Recovery boiler where black liquor is burned is also used for the regeneration of chemicals of the pulping process in addition to the energy production, and this might also have an effect on the environmental impacts. The error shown in the results is assumed to take into account the possible effect from the decisions made in the scope of this study.

5.4.1. Global warming potential

According to IPCC guidelines CO_2 emissions from combustion of biomass, for example biofuels, should be reported as zero for energy production (Rypdal et al. 2006, 1.6). Black liquor is listed as one of the biofuels (Gomez et al. 2006, 2.19) so this guideline is applied. Thus, the impact category selected from EF 3.0 is global warming potential that only takes into account fossil carbon and excludes biogenic carbon. As seen from figure 8, the GWP of the process without elemental sulfur is significantly lower than the process with elemental sulfur in all scenarios. The lowest it is when electricity is produced from black liquor: 25 kg CO_2 eq/t H_2SO_4 for SC5. With grid electricity, GWP is four times higher: 80 kg CO_2 eq/t H_2SO_4 for SC6. For the process that uses elemental sulfur, the impact is 142 kg CO_2 eq/t H_2SO_4 for SC1 and 187 kg CO_2 eq/t H_2SO_4 for SC2. The big difference is due to the GHG from the production of elemental sulfur which accounts for more than half of the impact in normal operation.

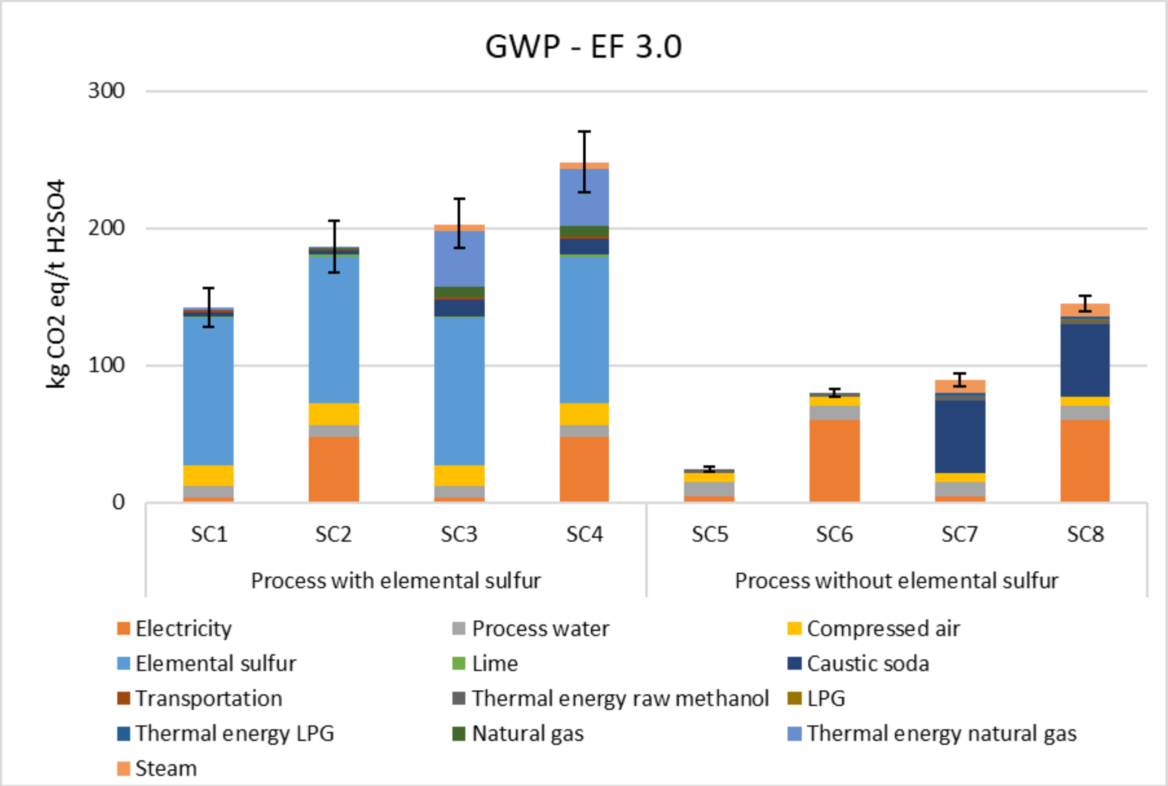


Figure 8. Global warming potential.

In addition to elemental sulfur, other main contributors in both process versions are electricity from grid and the production of process water and compressed air. In startup, the production of caustic soda is notable for the process without elemental sulfur. For the other process, the fossil fuel natural gas and especially its combustion increase the impact. Overall, the GWP of startup is higher in comparison to the normal operation but all scenarios of the process without elemental sulfur have lower impact than the process with it. The potentials of startup are 203 kg CO_2 eq/t H_2SO_4 for SC3, 248 kg CO_2 eq/t H_2SO_4 for SC4, 90 kg CO_2 eq/t H_2SO_4 for SC7 and 145 kg CO_2 eq/t H_2SO_4 for SC8.

5.4.2. Acidification potential

AP of both versions of the process are presented in figure 9. As shown in the figure, AP is higher for all scenarios when electricity is produced from black liquor rather than when it is from grid. This is due to the acidifying NOx emissions from biomass combustion. The lowest AP is for SC6: 0.49 mol H+ eq/t H_2SO_4. For SC5 is 0.61 mol H+ eq/t H_2SO_4. In comparison to the process without elemental sulfur, the difference is not very big. The impacts are 0.71 mol H+ eq/t H_2SO_4 for SC1 and 0.61 mol H+ eq/t H_2SO_4 for SC2. The main contributors in addition to electricity production are the production of elemental sulfur in the process where it is used and the combustion of raw methanol in the other process.

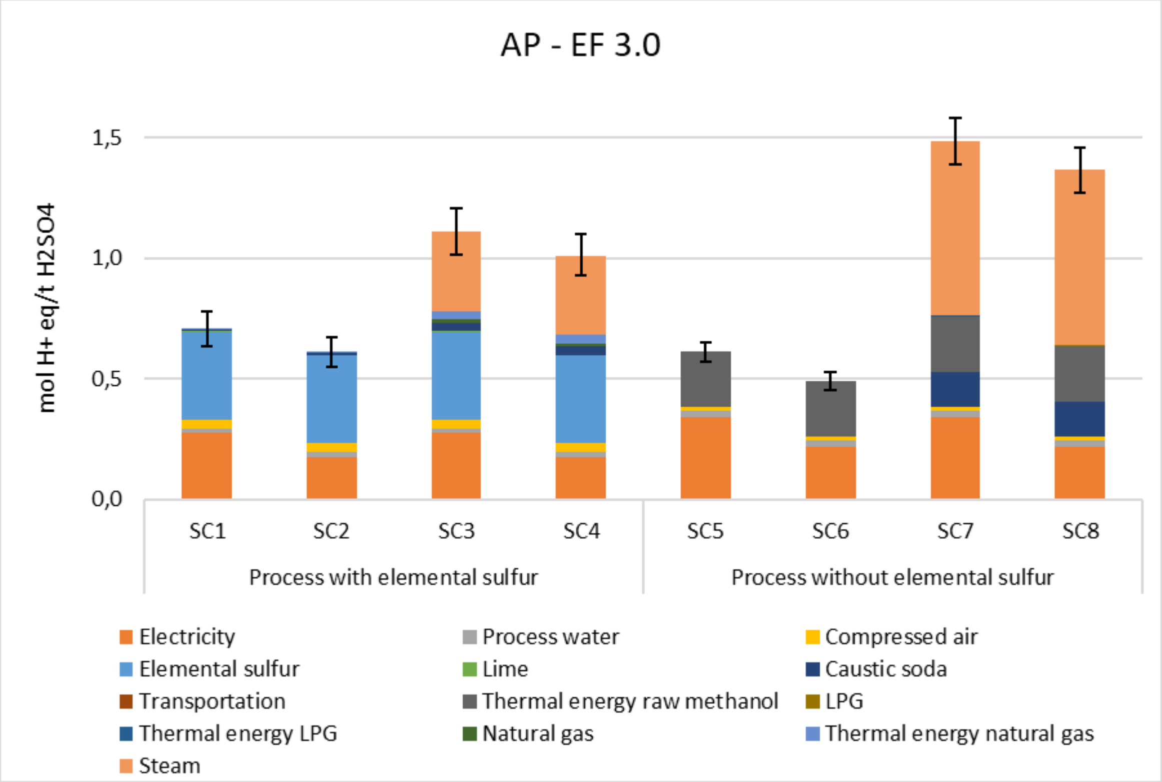


Figure 9. Acidification potential.

The potentials are higher in startup due to the production of steam. As steam is produced from black liquor, the NOx emissions of biomass combustion make the impact higher. For SC3 AP is 1.11 mol H+ eq/t H_2SO_4 and for SC4 1.01 mol H+ eq/t H_2SO_4 from which steam accounts for about a third. For the process without elemental sulfur, the impact of steam is more notable as it accounts for about half of the whole AP and raises it to be higher than for the process with elemental sulfur. AP is 1.49 mol H+ eq/t H_2SO_4 for SC7 and 1.37 mol H+ eq/t H_2SO_4 for SC8.

5.4.3. Eutrophication potential

In EF 3.0, eutrophication potential is given separately for freshwater and terrestrial, thus two figures are presented: freshwater EP in figure 10 and terrestrial EP in figure 11. As seen from the figure 10, freshwater EP is low for both versions of the process and for all scenarios. This is because the process has low sulfur and phosphorus emissions. Potential for SC5 is the lowest with $4.7 \cdot 10^{-4}$ kg P eq/t H_2SO_4. For SC6 the impact is $5.6 \cdot 10^{-4}$ kg P eq/t H_2SO_4 and the increase is due to electricity from grid. Mainly because of the production of caustic soda, in startup the freshwater EP is slightly higher: $6.9 \cdot 10^{-4}$ kg P eq/t H_2SO_4 for SC7 and $7.8 \cdot 10^{-4}$ kg P eq/t H_2SO_4 for SC8. Overall, the biggest contributor in all of the scenarios is the production of process water.

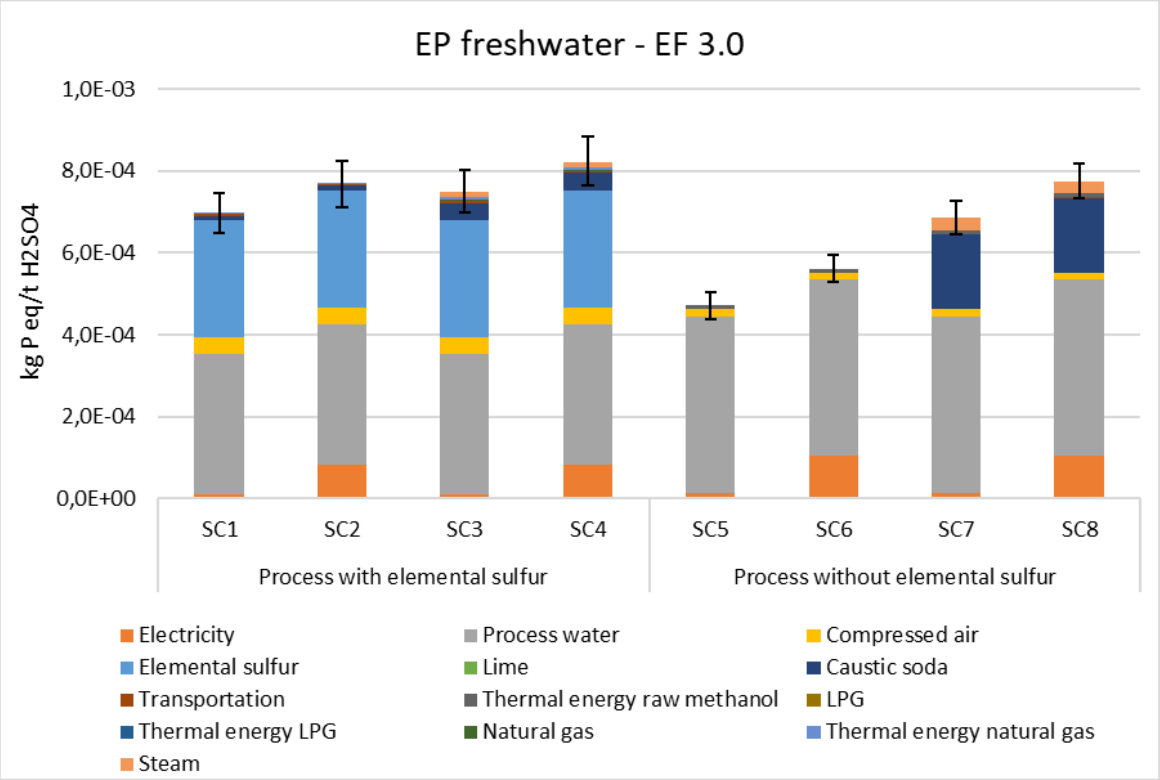


Figure 10. Eutrophication potential, freshwater.

For the process that uses elemental sulfur, the difference between the scenarios is even smaller. For SC1 freshwater EP is $7.0 \cdot 10^{-4}$ kg P eq/t H_2SO_4, for SC2 $8.0 \cdot 10^{-4}$ kg P eq/t H_2SO_4, for SC3 $7.5 \cdot 10^{-4}$ kg P eq/t H_2SO_4 and for SC4 $8.2 \cdot 10^{-4}$ kg P eq/t H_2SO_4. Similarly to the process without elemental sulfur, process water accounts for the biggest potential. In addition, the production of elemental sulfur has a notable contribution and that also why the freshwater EP is higher for this version of the process in comparison to when elemental sulfur is not used. The production of caustic soda is not as significant as in the process without elemental sulfur because it is used less. Due to this startup does not have notably higher freshwater EP.

For terrestrial EP, the potential is bigger when electricity is produced with black liquor instead of being from grid. The explaining reason can be the NOx emissions from biomass combustion. Opposite to freshwater EP, terrestrial EP is smaller for the process that uses elemental sulfur. The lowest impact is thus for SC2 with 1.2 mol N eq/t H_2SO_4. For SC1 it is 1.8 mol N eq/t H_2SO_4. Of the process without elemental sulfur, SC6 has the lowest potential with 1.5 mol N eq/t H_2SO_4. SC5 has the impact of 2.2 mol N eq/t H_2SO_4. The electricity production has overall quite notable effect on terrestrial EP and because the process without elemental sulfur uses more electricity, it has higher impact. Another main contributor is the combustion of raw methanol. In the modeling, thermal energy from biomass was used which includes NOx emissions. As raw methanol also contains nitrogen, it can be assumed it would also produce NOx emissions. Elemental sulfur is again one of the main contributors for the process that uses it.

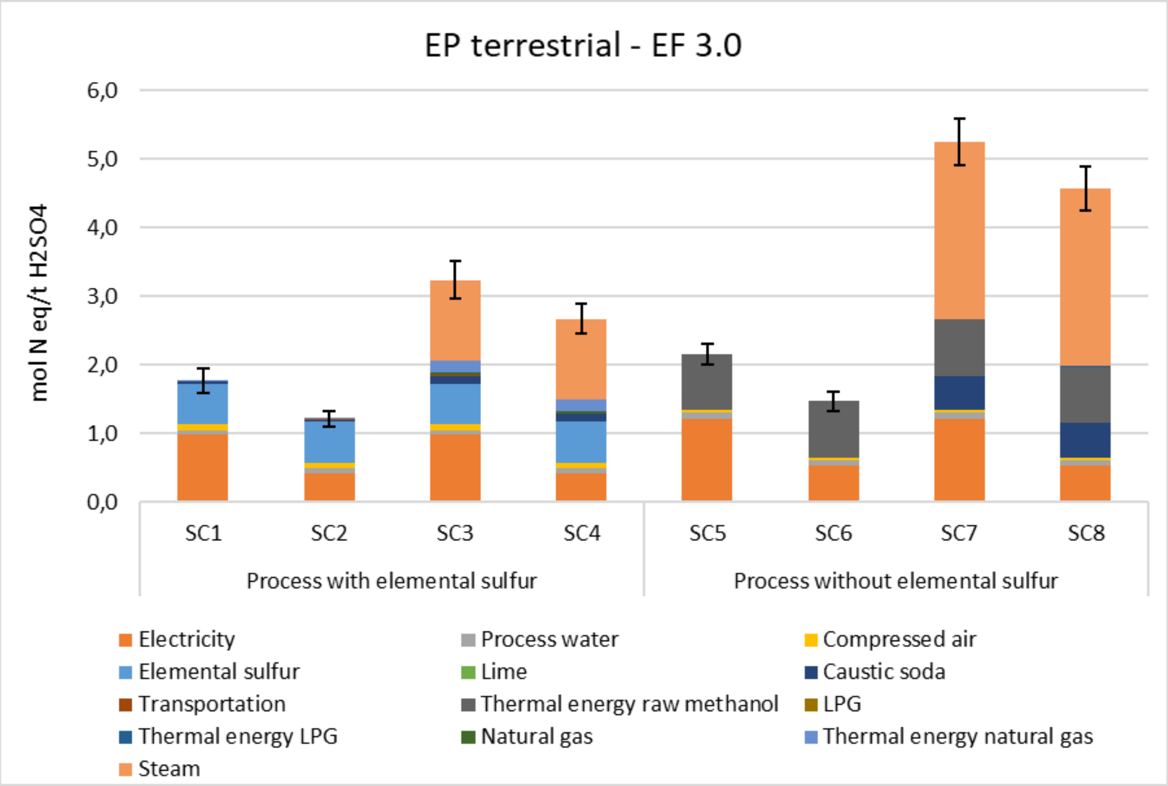


Figure 11. Eutrophication potential, terrestrial.

Startup has a bigger impact on terrestrial EP in comparison to freshwater EP and the main reason is the production of steam and its NOx emissions from black liquor combustion. For SC3 the potential is 3.2 mol N eq/t H_2SO_4 and for SC4 2.7 mol N eq/t H_2SO_4. Startup affects the process without elemental sulfur more notably as the results are 5.3 mol N eq/t H_2SO_4 for SC7 and 4.6 mol N eq/t H_2SO_4 for SC8. Steam production corresponds to about half of the impact.

5.4.4. Water depletion potential

WDP is presented in figure 12 and as it can be seen, process water contributes the most to WDP in all scenarios of both processes, over 95 %. Because process water accounts for most of the impact and is constant in the scenarios of each process, there are only very small differences between the scenarios. Overall, WDP of the process with elemental sulfur is smaller because less process water is needed in comparison to the process without elemental sulfur. The results for the process with elemental sulfur are 310 m^3 world eq/t H_2SO_4 for SC1 and 313 m^3 world eq/t H_2SO_4 for SC2. For startup the impacts are almost the same: 313 m^3 world eq/t H_2SO_4 for SC3 and 316 world m^3/t H_2SO_4 for SC4.

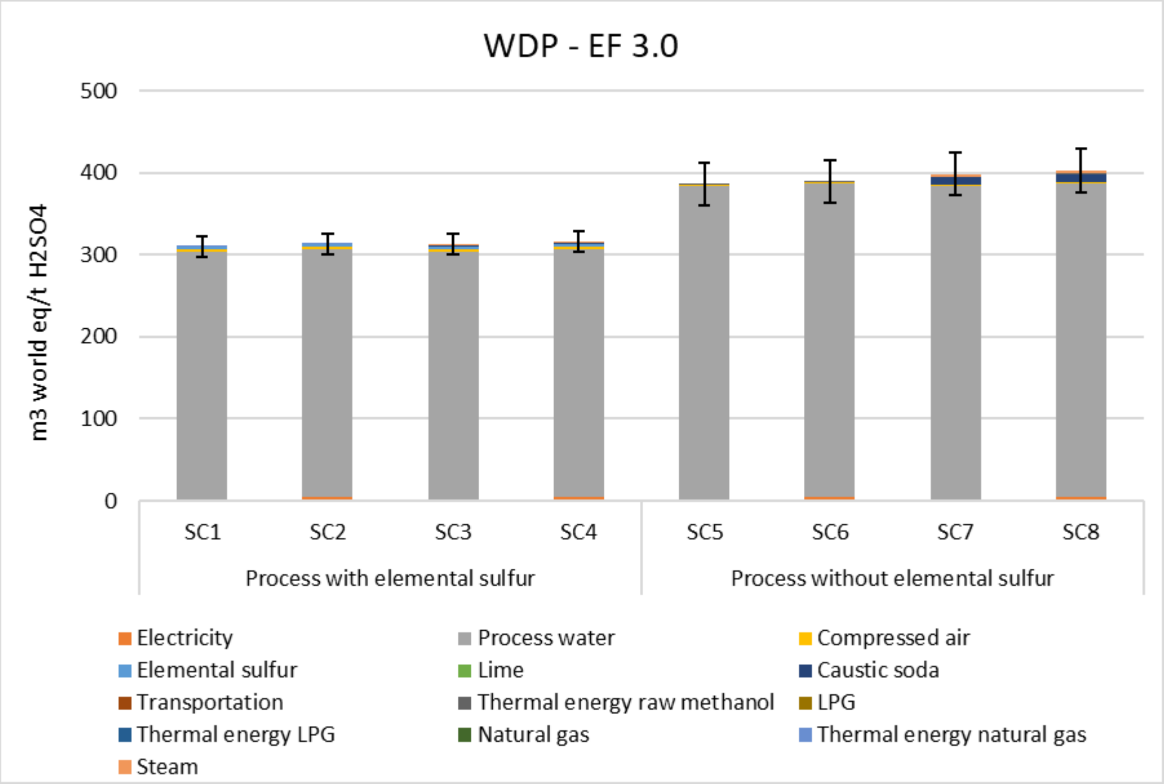


Figure 12. Water depletion potential.

The process that does not use elemental sulfur uses more process water per 1 ton of sulfuric acid, but the amount is not significantly higher. In WDP the difference can be seen between the processes but it is not very large. For SC5 the impact is 386 m^3 world eq/t H_2SO_4 and for SC6 389 m^3 world eq/t H_2SO_4. Similarly to the other process, the potential of startup is not very much higher in comparison to the normal operation. The results are 399 m^3 world eq/t H_2SO_4 for SC7 and 402 m^3 world eq/t H_2SO_4 for SC8.

5.4.5. Abiotic resource depletion potential

ADP is divided into minerals and metals and energy carriers in EF 3.0 and to present these two potentials, two figures are shown. As seen from figures 13, ADP of minerals and metals is low and varies between the scenarios. It follows a similar pattern as GWP with the process without elemental sulfur having the lowest impact in normal operation. The potential of SC5, $5.4 \cdot 10^{-6}$ kg Sb eq/t H_2SO_4, is significantly lower than the other scenarios of both processes. When electricity is from grid the potential more than doubles and SC6 has the potential of $1.3 \cdot 10^{-5}$ kg Sb eq/t H_2SO_4. Elemental sulfur has a notable impact on the process where it is used, and the potentials are higher: $2.1 \cdot 10^{-5}$ kg Sb eq/t H_2SO_4 for SC1 and $2.8 \cdot 10^{-5}$ kg Sb eq/t H_2SO_4 for SC2.

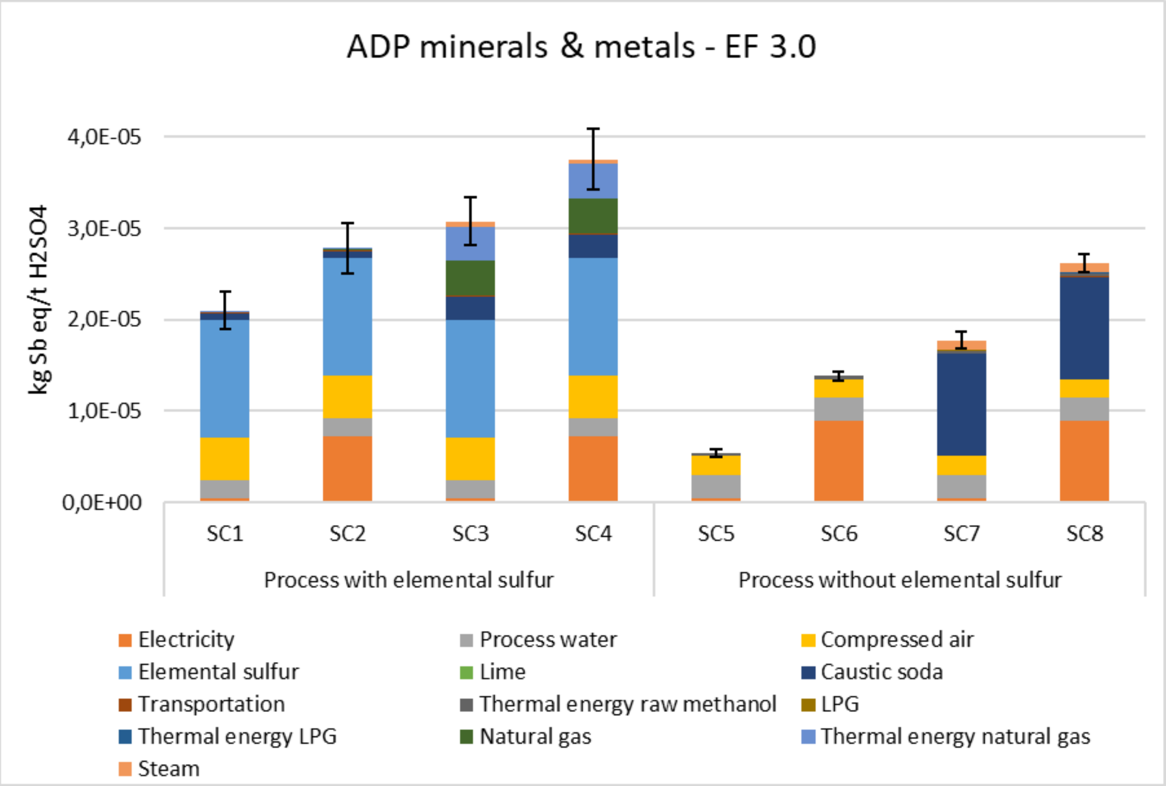


Figure 13. Abiotic resource depletion potential, minerals and metals.

In startup the production of caustic soda contributes largely to the increase of the impact. For the process without elemental sulfur caustic soda has a bigger effect making the potential for SC7 $1.8 \cdot 10^{-5}$ kg Sb eq/t H_2SO_4 and for SC8 $2.6 \cdot 10^{-5}$ kg Sb eq/t H_2SO_4. Still, for the process with elemental sulfur, the potentials are higher: $3.1 \cdot 10^{-5}$ kg Sb eq/t H_2SO_4 for SC3 and $3.8 \cdot 10^{-5}$ kg Sb eq/t H_2SO_4 for SC4. In addition to caustic soda, the production and combustion of natural gas increase the impact in comparison to normal operation.

As seen from figure 14, there is a clear difference between the two processes on ADP of energy carriers. For the process that uses elemental sulfur, ADP of energy carriers is significantly higher mainly because of the use of elemental sulfur which accounts for 62-90 % of the impact depending on the scenario. Overall, for the process with elemental sulfur ADP of energy carriers is high in all of the scenarios: 5967 MJ/t H_2SO_4 for SC1, 7160 MJ/t H_2SO_4 for SC2, 7474 MJ/t H_2SO_4 for SC3 and 8668 MJ/t H_2SO_4 for SC4. Fossil fuels are the main contributors thus electricity from grid and the use of natural gas in startup increase the potential.

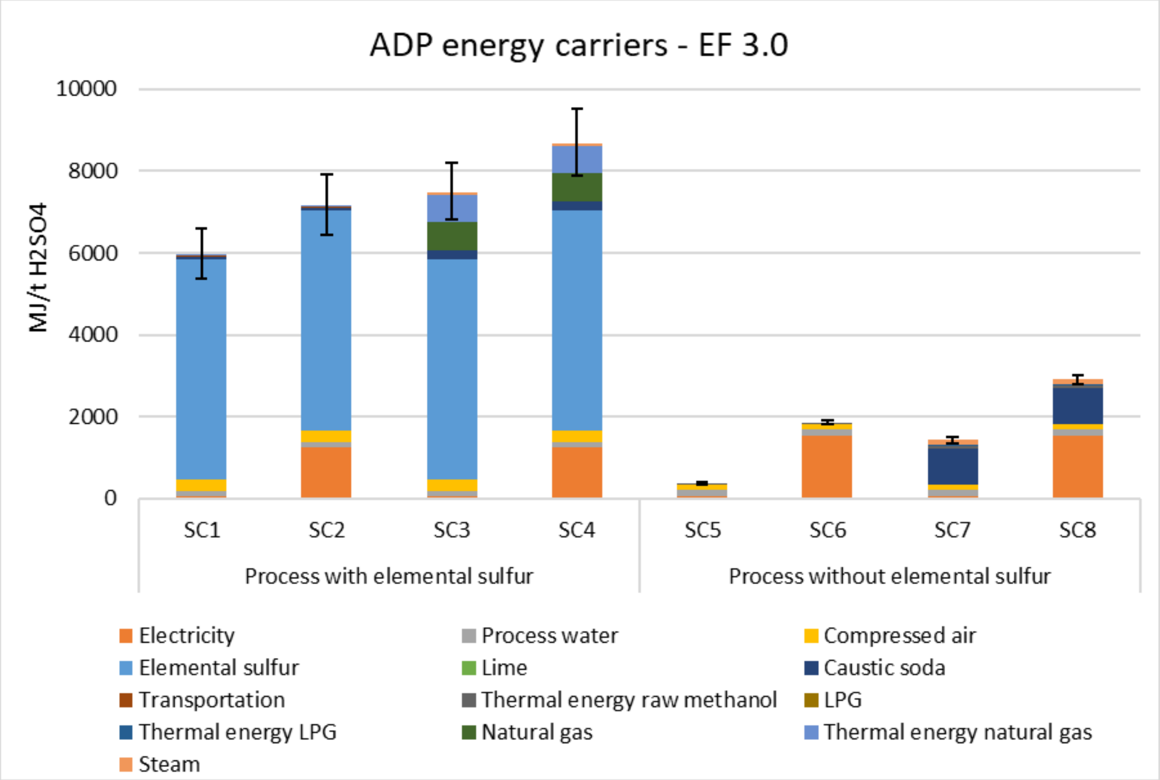


Figure 14. Abiotic resource depletion potential, energy carriers.

In the process where elemental sulfur, ADP of energy carriers is small, especially for the SC5 when electricity is from black liquor. The potential of SC5 is 383 MJ/t H_2SO_4, only 6 % of the potential of SC1. For SC6 electricity from grid makes the potential almost five times higher to 1863 MJ/t H_2SO_4. In startup the results are 1436 MJ/t H_2SO_4 for SC7 and 2915 MJ/t H_2SO_4 for SC8. The production of caustic soda and electricity from grid are the main contributors.

5.4.6. Human toxicity potential

In EF 3.0, two HTP values can be obtained: one with carcinogenic effects and one with non-carcinogenic effects. The substances affecting carcinogenic HTP from the impacting processes are hydrocarbons as well as non-methane volatile organic compounds (NMVOCs) which can produce carcinogenic compounds. In figure 15, the HTP with carcinogenic effects is presented and it can be seen that the potential is relatively low. The difference between the impact of the two electricity production methods is very small which is why the potentials of normal operation scenarios as well as startup scenarios are almost the same. The result of SC5 is overall the lowest with $3.4 \cdot 10^{-8}$ CTUh/t H_2SO_4. For SC6 it is $3.6 \cdot 10^{-8}$ CTUh/t H_2SO_4. The main contributors are the electricity production and combustion of raw methanol. For the process with elemental sulfur the impact is notably higher with the potential of $9.3 \cdot 10^{-8}$ CTUh/t H_2SO_4 for SC1 and $9.5 \cdot 10^{-8}$ CTUh/t H_2SO_4 for SC2. The production of elemental sulfur corresponds to over 75 % of the impact.

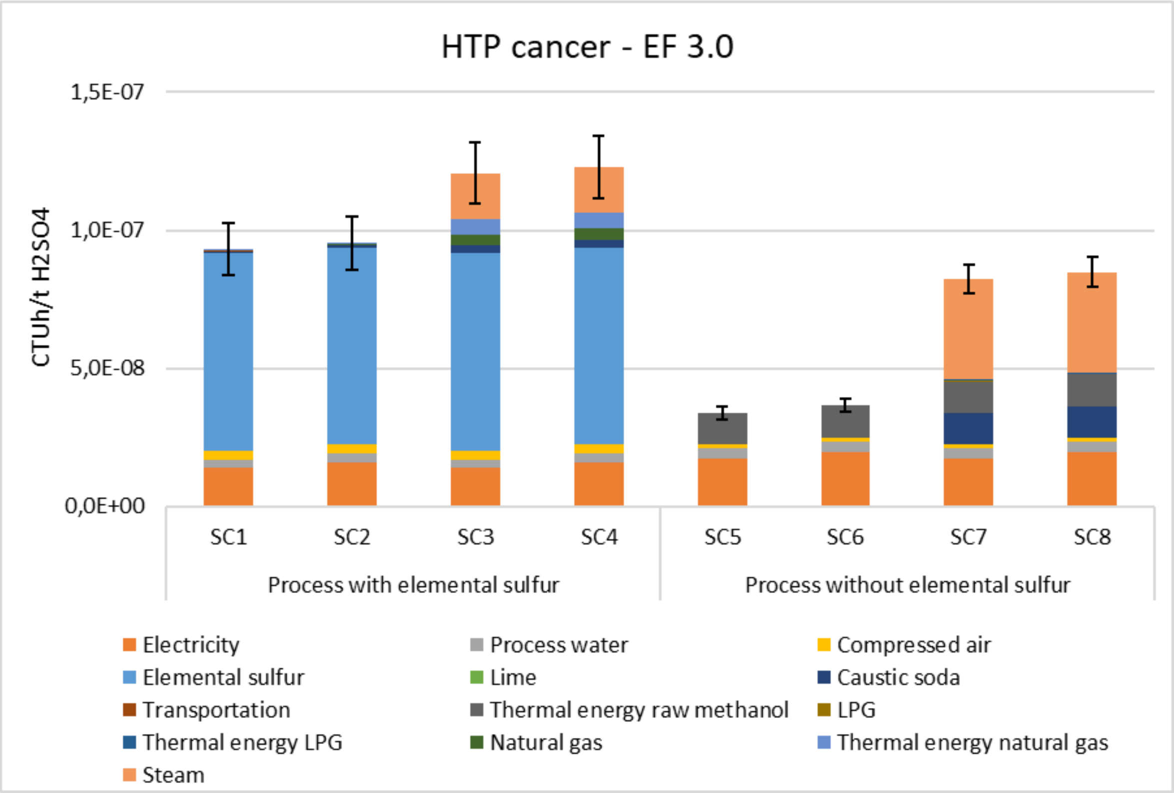


Figure 15. Human toxicity potential, cancer.

Startup potentials are mainly affected by the production of steam. For SC3 carcinogenic HTP is $2.1\cdot10^{-7}$ CTUh/t H_2SO_4 and for SC4 $2.3\cdot10^{-7}$ CTUh/t H_2SO_4. The use of natural gas also play a role. For the process that does not use elemental sulfur, steam has a bigger effect and also the production of caustic soda contributes making the potential of SC7 $8.2\cdot10^{-8}$ CTUh/t H_2SO_4 and SC8 $8.5\cdot10^{-8}$ CTUh/t H_2SO_4.

HTP with non-carcinogenic impacts is presented in figure 16. Affecting substances from the processes to the non-carcinogenic HTP are particulate matter (PM) especially >PM10, heavy metals and NMVOCs. As seen from the figure, non-carcinogenic HTP is higher than carcinogenic HTP but the differences between the scenarios follow a similar pattern. For non-carcinogenic HTP electricity production method, however, has a bigger effect and when electricity is from black liquor, the potential is higher. The lowest potential is thus for SC6 with $1.9\cdot10^{-6}$ CTUh/t H_2SO_4. For SC5 it is $2.6\cdot10^{-6}$ CTUh/t H_2SO_4. The combustion of raw methanol in addition to electricity and process water production are the main contributors.

For the process with elemental sulfur, SC2 has the smallest impact: $4.1 \cdot 10^{-6}$ CTUh/t H_2SO_4 while SC1 has the impact of $4.6 \cdot 10^{-6}$ CTUh/t H_2SO_4. Similarly, to carcinogenic HTP, in this case also elemental sulfur is a main contributor. For the process without elemental sulfur, SC6 has the smallest impact with $4.8 \cdot 10^{-6}$ CTUh/t H_2SO_4. The potential of SC5 is $5.6 \cdot 10^{-6}$ CTUh/t H_2SO_4.

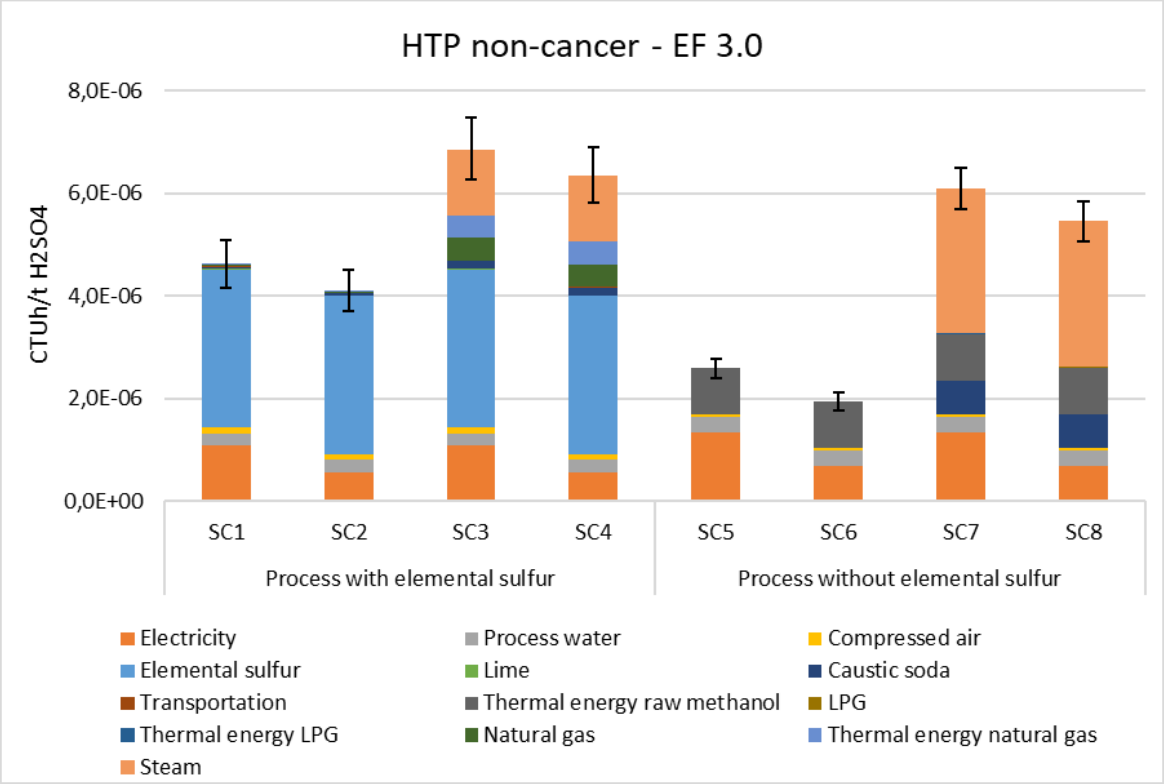


Figure 16. Human toxicity potential, non-cancer.

In startup, the potentials are higher, and for the process without elemental sulfur the difference between startup and normal operation is more notable. This is mainly due to the steam production but caustic soda also affect. For SC7 the potential is $6.1 \cdot 10^{-6}$ CTUh/t H_2SO_4 and for SC8 $5.5 \cdot 10^{-6}$ CTUh/t H_2SO_4. For the process with elemental sulfur, steam also increases the potential but not as much as for the other process. Non-carcinogenic HTP of SC3 is $6.9 \cdot 10^{-6}$ CTUh/t H_2SO_4 and SC4 $6.3 \cdot 10^{-6}$ CTUh/t H_2SO_4.

6. Discussion

This chapter presents the discussion of the study and the results. First the results are compared to two previous LCA studies of sulfuric acid production. Then the study is discussed in a broader view.

6.1. Comparison of the results to previous studies

The results of the baseline scenarios of this study are compared to LCA studies by Marwa et al. (2017) and Adeniran et al. (2017). These two studies are conducted for the production of sulfuric acid from elemental sulfur. Since the studies include some differences in their scope, the main contents of the scopes of the studies and the baseline scenarios SC1 and SC5 are gathered in table 14.

Table 14. Similarities and differences in the scopes of SC1, SC5 and previous LCA studies.

	SC1	**SC5**	**Marwa et al. 2017**	**Adeniran et al. 2017**
Location	Finland	Finland	Tunisia	Nigeria
Life cycle stages	Sulfuric acid production, material and energy production, transportation	Sulfuric acid production, material and energy production, transportation	Sulfuric acid production, energy production, transportation, equipment	Sulfuric acid production, material and energy production
Sulfur preparation	Included	Not needed in the process	Included	Included
Sulfur source	CNCG and elemental sulfur	CNCG	Elemental sulfur	Elemental sulfur
Electricity source	Black liquor	Black liquor	Steam and natural gas	US grid
Water	Demineralized water	Demineralized water	Not specified	Demineralized water
Transport	Road transport: elemental sulfur, caustic soda, lime, filter residue	Road transport: caustic soda, LPG	Road and sea transport: elemental sulfur, catalyst, chemical consumables, equipment	Not taken into account

To compare this study to the previous to the studies by Marwa et al. (2017) and Adeniran et al. (2017), the results are presented in table 15. The results of the two previous studies are from the original sources but they are converted to represent the functional unit of 1 ton of produced sulfuric acid. The results of SC1 and SC5 are presented in comparable units based on the units that were used in the previous studies. The study by Marwa et al. (2017) did not include all the impact categories selected for this assessment but the comparison is done for those that were included. Adeniran et al. (2017) did not present freshwater and terrestrial EP but instead an overall EP.

Table 15. Environmental impacts compared to two previous LCA studies of sulfuric acid production.

Impact category	**SC1**	**SC5**	**Marwa et al. 2017**	**Adeniran et al. 2017**
GWP (kg CO_2 eq/t H_2SO_4)	142	25	89	270
AP (mol H+ eq/t H_2SO_4)	0.71	0.61	4.0	-
AP (kg SO_2 eq/t H_2SO_4)	0.64	0.59	-	4.4
EP (kg Phosphate eq/t H_2SO_4)	0.065	0.071	-	0.14
EP fresh water (kg P eq/t H_2SO_4)	$7.0 \cdot 10^{-4}$	$4.7 \cdot 10^{-4}$	$12 \cdot 10^{-3}$	-
EP terrestrial (mol N eq/t H_2SO_4)	1.8	2.2	1.8	-
WDP (m^3/t H_2SO_4)	7.4	9.2	-	37
ADP minerals&metals (kg Sb eq/t H_2SO_4)	$2.1 \cdot 10^{-5}$	$5.4 \cdot 10^{-6}$	-	$1.2 \cdot 10^{-4}$
ADP energy carriers (MJ/t H_2SO_4)	5967	383	-	9700
HTP (1,4-DB eq/t H_2SO_4)	29	3.2	-	16

As seen from the table, SC5 has significantly lower GWP in comparison to SC1 and the previous studies. Especially the difference can be seen when comparing SC5 to SC1 and the study by Adeniran et al. (2017). In both of the studies, sulfuric acid is produced from elemental sulfur by-product from oil or gas refineries. In the study by Marwa et al. (2017), it is not however clearly stated whether or not the production of elemental sulfur is taken into account in the system boundary or not. Because the GWP is quite notable lower than in SC1 the study by Adeniran et al. (2017) where elemental sulfur is used, it would be sensible to assume that elemental sulfur is not taken into account. That would explain why the GWP is lower. However, in relation to EP, Marwa et al. (2017) mention petroleum desulfurization as one of the contributors which leads to the assumption that the production of elemental sulfur is part of the system boundary.

In the study by Adeniran et al. (2017), 99 % of the GWP is from elemental sulfur and in SC1 75 %. In the study by Adeniran et al. (2017), only elemental sulfur is used as the sulfur input whereas in SC1 it is the additional input to support CNCG which is why the GWP of SC1 is lower. In the study by Marwa et al. (2017), the main contributor to GWP is sulfur treatment which would support the assumption that the production of elemental sulfur is not considered. If it is considered, it is not clear why elemental sulfur does not affect GWP more.

Another affecting factor is the electricity production. Adeniran et al. (2017) with higher GWP use the United States grid for electricity while SC1 with lower GWP use black liquor. Marwa et al. (2017) use both excess steam from the sulfuric acid process and natural gas for electricity production. If elemental sulfur is not taken into account, the use of natural gas could explain why the study has higher impact than SC5. But if elemental sulfur is part of the system boundary, it cannot be said why the GWP is lower in comparison to SC1 and Adeniran et al. (2017) even though in addition to elemental sulfur use, electricity is produced by a fossil fuel instead of renewable source like in SC1.

AP of SC1 and SC5 are notably lower in comparison to both of the previous studies. In the study by Adeniran et al. (2017), AP was due to SOx emissions from the production of elemental sulfur, electricity and the plant. Direct emissions from the plant contribute for 72 % (Adeniran et al. 2017). Similarly, in the study by Marwa et al. (2017), SOx emissions from the plant was the biggest contributor to AP. Flue gas treatment was given as a solution for lowering the AP (Marwa et al. 2017) so cleaning of flue gases is not considered in the study. For SC1 and SC5, there is flue gas cleaning at the plant and SOx emissions from the plant are assumed to be almost non-existent which explains why AP is so much smaller in comparison to the other studies.

When examining the freshwater and terrestrial EP from the study by Marwa et al. (2017), it can be seen that freshwater EP is significantly higher in comparison to SC1 and SC5. Marwa et al. (2017) do not explain what contributes to freshwater EP other than the sulfuric acid production process which can include both sulfur pre-treatment and the actual process. It could be assumed that the process by Marwa et al. (2017) has more phosphorous emissions to water than SC1 and SC5.

Terrestrial EP on the other hand is at a similar level as in the study by Marwa et al. (2017). For SC1 it is the same but for SC5 a bit higher. Marwa et al. (2017) state the main contributors for terrestrial EP to be the N emissions from natural gas combustion and petroleum desulfurization. Because the desulfurization is mentioned here, it gives the impression that the production of elemental sulfur is part of the system boundary. Similarly, for SC1 the biggest contributors are the electricity production and elemental sulfur. SC5 does not have elemental sulfur but electricity production and raw methanol combustion contribute. Adeniran et al. (2017), used overall EP that does not divide the potential to freshwater and terrestrial potential. EP of both SC1 and SC5 is about half of the one from that study. The biggest contribution to EP in the study by Adeniran et al. (2017) was the production of elemental sulfur.

For WDP, SC1 and SC5 are much lower in comparison to the study by Adeniran et al. (2017). This can be explained by the fact that the WDP used in the study by Adeniran et al. (2017) takes into account both water availability and pollution whereas in this study only water scarcity was assessed. Adeniran et al. (2017) state that WDP is mostly affected by direct emissions from the production of sulfuric acid and the production of process water only contributed by 9 % (Adeniran et al. 2017). If pollution was not taken into account, that remaining 9 % would be lower than in SC1 and SC5. In the process from Adeniran et al. (2017), the amount of water produced for the process is very small.

When comparing the ADP of minerals and metals, it can be seen that for both scenarios of this study the potential is notably lower than in the study from Adeniran et al. (2017). ADP of mineral and metals of the study by Adeniran et al. (2017) is 6 times higher than SC1 and more than 20 times higher than SC5. The biggest contributor in the study by Adeniran et al. (2017) was elemental sulfur followed by process water. The impact could be higher due to the higher amount of elemental sulfur used in comparison to SC1. This could also explain why SC5 has so much lower impact as no elemental sulfur is used.

ADP of energy carriers is also lower for both scenarios. In comparison to SC1, the potential of the study by Adeniran et al. (2017) is more than 1.5 times higher. For SC5 the difference is very significant as the ADP of energy carriers is about 25 times higher. Adeniran et al. (2017) do not specify what affects the potential other than the production process but elemental sulfur and grid electricity are likely to have a big impact. This is likely as there is also such a big difference between SC1 and SC5 and only SC1 uses elemental sulfur.

The carcinogenic and non-carcinogenic HTP are summed together to get overall HTP for SC1 and SC5. The potential of SC1 is almost twice as high as in the study from Adeniran et al. (2017). SC5, however, has significantly lower impact in comparison to both SC1 and Adeniran et al. (2017). The corrosiveness of the on-site infrastructure as well as the concentration of sulfuric acid is explained to be the biggest contributor to HTP. However, looking at the figure of the HTP results of the study by Adeniran et al. (2017), it is seen that elemental sulfur accounts for all or most of the potential.

The previous LCA studies were selected based on the possibility to compare them to the results of this study. Because there is a lack of LCA studies of sulfuric acid production, only two studies were able to be compared and the system boundaries were varying. In the future, it would be valuable to conduct LCA studies of sulfuric acid production that had the same system boundaries so the environmental impacts of different production methods could be compared more effectively and precisely.

6.2. Discussion of the study

This study assessed the environmental impacts of sulfuric acid manufacturing process from CNCG of Kraft pulping process. It was examined how the impacts differ for two versions of the process. Overall, in most of the studied impact categories, the process that uses elemental sulfur as an additional sulfur input has higher environmental impacts than the process where it is not used. Thus, from the environmental point of view, it would be better to produce sulfuric acid from CNCG without additional sulfur input. Pulp mills produce 2-7 kg/ADt of sulfur in odorous gases (Mahecha-Botero et al. 2021, 103; Valmet 2017, 5) and based on the amounts of substance and molar masses, 327 kg of sulfur is needed in the production of 1 ton of sulfuric acid. The theoretical capacity to produce sulfuric acid from odorous gases at pulp mill is then 6-21 kg H_2SO_4/ADt. In Finland, about 8 million tons of pulp is produced annually (Metsäteollisuus 2022), meaning theoretically 49 000-171 000 t H_2SO_4 could be manufactured yearly.

Another limiting factor in the use of elemental sulfur is the estimated shortage of by-product elemental sulfur from the oil and gas industries. In the sulfuric acid production process, elemental sulfur is used as a support sulfur input and its benefits are in the higher produced sulfuric acid yield. The process also consumes less some of the needed materials such as process water and steam per sulfuric acid ton. However, when elemental sulfur is not used, other inputs like compressed air and electricity are needed less per ton of sulfuric acid. The process with elemental sulfur also has an additional process step where the sulfur is pre-treated.

If additional sulfur input is needed, replacing the elemental sulfur from refineries could be a solution. Pulp mills produce sulfurous wastewater where sulfur can be recovered from. Because recovery methods like Claus and amine-process are energy-intensive and cause corrosion, biological recovery has gained interest. (Hajdu-Rahkama & Puhakka 2022, 1.) Biological sulfur recovery can be done with two-step process the sulfur compounds are reduced to H_2S with sulfur reducing bacteria and then oxidized to S (Janssen et al. 2009, 1335; Hajdu-Rahkama & Puhakka 2022, 1). Another method is oxidation of sulfur compounds with chemolithoautotrophic sulfur oxidizing bacteria (Hajdu-Rahkama & Puhakka 2022, 1). The sulfur recovered from pulp mill wastewater could be used for replacing the elemental sulfur from refineries. The properties of biologically recovered sulfur, however, are not completely like inorganically produced sulfur (Janssen et al. 2009, 1341). The recovery rate of sulfur from wastewater is affected by the organic composition of the wastewater (Hajdu-Rahkama & Puhakka 2022, 5). The suitability of biologically produced sulfur for the production of sulfuric acid should be further studied.

In this study, the energy production was selected to contain mainly biobased energy. The differences between electricity production methods were studied by comparing black liquor combustion and grid electricity. As seen from the results, the usage of black liquor for electricity production decreased the impacts in most of the studied impact categories in comparison to grid electricity. An uncertainty related to the use of black liquor comes from whether there is enough of energy for the production of sulfuric acid at a pulp mill. In this case, the pulp mill does not have paper production plant integrated and it was assumed the energy from black liquor would be sufficient for sulfuric acid plant because in some pulp mills energy is produced for external use in addition to the pulp mill itself (Mäki et al. 2021, 1). However, if the plant was an integrated pulp and paper production plant, it is not clear whether there would be enough energy production from just black liquor to cover the production of sulfuric acid.

The energy production in this study was not fully renewable as some fossil fuels were used: natural gas in mist control and startup as well as LPG as a startup fuel. Replacing these fossil fuels could reduce the environmental impacts in many impact category like seen in electricity production. Promising alternatives for fossil fuels are biofuels produced internally at pulp mills such as tall oil (Aro & Fatehi 2017, 470; Mäki et al. 2021, 4) and green methanol (Mäki et al. 2021, 4; Pio et al. 2022, 5403). Tall oil by-production from the Kraft pulping process is already commercialized and crude oil and its purified fractions can be used as fuel (Aro & Fatehi 2017, 470). Green methanol can be produced at pulp mill from by-products or from stripper off gases (Pio et al. 2022, 5403). It is already used at pulp mills (ANDRITZ 2022) which is why it was used in this study. Raw pulp mill methanol contains nitrogen and sulfur which lead to emissions and in order to reduce these emissions, methanol purification has been developed (ANDRITZ 2022). Purified methanol could have been selected instead of LPG but due to a lack of information available on the environmental impacts of purified methanol, it was not used in this study.

In addition to the selection of energy production method, optimizing the sulfuric acid production process and the amount of energy and materials is important. Depending on the input and output values, the results show quite notable differences in the environmental impacts. At best the environmental impacts show to be lower in many impact categories in comparison to the production of sulfuric acid from elemental sulfur but higher amount of energy and materials consumption lead to higher potential impacts. It should also be considered that the environmental impacts during startup are higher due to the additional inputs, but whether or not it is significant depends on the frequency of the plant’s run downs and startups.

In future research it would be beneficial to study how the sulfuric acid production plant affects the environmental impacts of a pulp mill. For that purpose, an LCA study of a whole pulp mill including the production of pulp and by-products should be done. By considering the whole pulp mill, it would be possible to study aspects like energy and chemical recovery as well as the sulfur cycle and Na/S balance. Sulfuric acid production reduces the need for removing sulfur from the pulping process and thus solid waste generation and ash dumping. The environmental benefits of these could be studied with a broader study. A comparison study could be conducted of a mill with and without sulfuric acid production in order to examine the benefits of sulfuric acid production. For example, there are possible benefits from utilizing the excess steam from the sulfuric acid process in pulp and paper production. It could also be studied whether the internal energy production from black liquor combustion would be enough for sulfuric acid production in addition to an integrated pulp and paper mill.

Studying the water related impacts of sulfuric acid production in more detail could also be relevant as the process uses considerably large amounts of water. This study took into account water depletion potential as water scarcity but by conducting a comprehensive water footprint assessment also water degradation footprint and water availability footprint could be studied. In water footprint study the water flows excluded from this study, such as cooling water or wastewater, could be examined. In this study, the production location was Finland where water consumption is considered not to be an issue but in locations where it is more critical, conducting a comprehensive water footprint assessment would be more relevant.

7. Conclusions

Production of sulfuric acid from odorous gases of Kraft pulp mill could be an alternative to the currently predominant production method that uses elemental sulfur from gas and oil refineries. As the production of fossil fuels is decreasing due to climate change mitigation, elemental sulfur can become shortage which is why alternative production methods are needed. Using CNCG as the sulfur input could be a promising alternative as the environmental impacts are lower in most of the impact categories studied in this LCA in comparison to the production from elemental sulfur. Elemental sulfur can be used as an additional sulfur input with CNCG from pulp mill. However, the results of this study show that the environmental impacts are lower for most of the studied impact categories when elemental sulfur is not used. Using additional sulfur input can be beneficial for higher product yield and lower impacts in terrestrial eutrophication and water depletion. For this purpose, elemental sulfur could be replaced with another sulfur input, possibly a side stream from the pulping process.

Sulfuric acid production could also bring advantages to the pulping process itself as it can simultaneously act as a method for odorous gas treatment and sulfidity control. By replacing the typical sulfidity control method, ash dumping, with sulfuric acid production, advantages could be gained. These benefits are reduced solid waste ash production and landfilling, reduced need for sodium makeup chemical, savings and additional revenue. Integrating a sulfuric acid plant to a pulp mill also supports the current development trend of side stream utilization in the pulping industry.

8. Summary

This thesis examined the environmental impacts of sulfuric acid production from concentrated non-condensable gases of Kraft pulping process by conducting a life cycle assessment study. The results of the life cycle assessment were compared to previous studies of sulfuric acid manufacturing. The theoretical part of this thesis was a literature review focusing on background information about sulfuric acid and Kraft pulping that supported the empirical part. The subjects presented were sulfuric acid market, sulfur in Kraft pulping and sulfuric acid production. The chapter regarding sulfur in Kraft pulping included information about the Kraft pulping process, its sulfur balance and non-condensable gases. The production process of sulfuric acid that was studied in the empirical part was introduced. In addition to the production at pulp mill, it was presented how sulfuric acid is produced in other industries.

The empirical part consisted of the life cycle assessment study done based on the ISO 14040 and 14044 LCA methodology. The product system was a WSA production plant at a non-integrated softwood Kraft pulp mill. Two versions of the process were modelled, and their impacts compared to one another as well as to previous LCA studies of sulfuric acid production. Startup of the plant and different electricity production methods were considered in different scenarios. The impact categories studied in the LCA were global warming potential, acidification potential, eutrophication potential, water depletion potential, abiotic resource depletion potential and human toxicity potential.

The results of the study showed that the environmental impacts of the process without elemental sulfur were lower in all impact categories other than terrestrial EP and WDP. The main contributors to the impacts depended on the process and scenario. Notable inputs were electricity and process water. Biggest contribution to the impacts of the process with additional sulfur input was in most impact categories the production of elemental sulfur. In the process without elemental sulfur, the largest contributors were the not as clear. Transportation, lime, natural gas for mist control and LPG had minimal impacts in all categories. In startup, steam, natural gas and caustic soda had notable impacts in many categories.

In comparison to two previous LCA studies of sulfuric acid production, the environmental impacts of this study were lower in most of the studied impact categories. The results of the process with only CNCG as the sulfur input were lower than the compared studies in every category except for terrestrial EP. GWP was notably lower than in the previous studies. For the process with additional elemental sulfur, the results also showed lower environmental impacts than the compared studies in impact categories other than HTP and GWP. The GWP however was lower than one of the studies but higher than the other. Overall, in comparison to sulfuric acid production from elemental sulfur, using CNCG from pulping process show lower environmental impacts in GWP, AP, freshwater EP, WDP, ADP and HTP.

References

Abumounshar, N.M. et al. 2021. A detailed reaction mechanism for elemental sulphur combustion in the furnace of sulphuric acid plants. The Canadian Journal of Chemical Engineering, vol. 99, no. 11, pp. 2441-2451. DOI: https://doi.org/10.1002/cjce.24185

Adeniran, J.A. et al. 2017. Life Cycle Engineering Case Study: Sulphuric Acid Production. Journal of Engineering and Technology, vol. 8, no. 2, pp. 1-22. ISSN: 2180-3811.

Agribalyse. 2020. Life Cycle Assessment Method. [Online publication]. [Cited 2022-10-14]. Available: https://doc.agribalyse.fr/documentation-en/agribalyse-data/life-cycle-assessment-method

Alen, R. 2015. Pulp Mills and Wood-Based Biorefineries. In book: Pandey, A. et al. (edit.). Industrial Biorefineries and White Biotechnology. Elsevier. ISBN: 978-0-444-63453-5.

Amiri, M & Alihosseinpour, H. 2015. Identification of Metallurgical Sulphuric Acid Plants Production Line Bottlenecks. International Journal of Mechanical And Production Engineering, vol. 3, no. 10, pp. 88-93. ISSN: 2320-2092.

ANDRITZ. n.d. Kraft pulp. [Online publication]. [Cited 2022-05-16]. Available: https://www.andritz.com/pulp-and-paper-en/pulp-production/kraft-pulp-overview

ANDRITZ. 2022. A-Recovery+ chemical recovery concept for methanol purification in kraft mills. [Online publication]. [Cited 2022-10-19]. Available: https://www.andritz.com/products-en/group/pulp-and-paper/pulp-production/kraft-pulp/a-recovery-plus/methanol-purification

ANDRITZ GROUP. 2022a. Figure of WSA process. [Unpublished confidential figure].

ANDRITZ GROUP. 2022b. WSA LCA. [Unpublished confidential PDF document].

Aro, T. & Fatehi, P. 2017. Tall oil production from black liquor: Challenges and opportunities. Separation and Purification Technology, vol. 175, pp. 469-480. DOI: https://doi.org/10.1016/j.seppur.2016.10.027

Atanasova, L.G. 2017. Exery analysis of the process of regeneration of spent sulphuric acid by WSA technology. International Journal of Exergy, vol. 24, no. 1, pp. 57-81. DOI: https://doi.org/10.1504/IJEX.2017.086860

Athena Information Solutions Pvt. Ltd. 2020. Market Report: Surge in Sulphuric Acid Market in Asia. Chemical Industry Digest, pp. 1-2. ISSN: 09715266.

Bajpai, P. 2018. Pulping fundamentals. In book: Bajpai, P. Biermann’s Handbook of Pulp and Paper: Raw Material and Pulp Making. Third Edition. Elsevier. ISBN: 978-0-12-814240-0.

Back, S. 2019. Finnish pulp and paper industry is on the move. [Online publication]. [Cited 2022-10-05]. Available: https://www.paperadvance.com/blogs/soeren-back/finnish-pulp-and-paper-industry-is-on-the-move.html

Benvenuto, M.A. 2015. Sulfuric Acid Production, Uses, Derivatives. In book: Benvenuto, M.A. Industrial Inorganic Chemistry. De Gruyter, Berlin, Germany. ISBN: 978-3-11-033032-8.

Bijok, N. et al. 2022. Modelling the kraft pulping process on a fibre scale by considering the intrinsic heterogeneous nature of the lignocellulosic feedstock. Chemical Engineering Journal, vol. 438, p. 135548. ISBN: 1385-8947.

Brimblecombe, P. 2003. Biochemical Cycles: Sulfur Cycle. In book: Pyle, J. et al. (edit.). 2015. Encyclopedia of Atmospheric Sciences, 6 Volume Set (The Second Edition). Elsevier. ISBN: 978-0-12-382225-3.

Eckelman, M.J. 2016. Life cycle inherent toxicity: a novel LCA-based algorithm for evaluating chemical synthesis pathways. Green chemistry: an international journal and green chemistry resource, vol. 18, no. 11, pp. 3257-3264. DOI: https://doi-org.ezproxy.cc.lut.fi/10.1039/C5GC02768C

Ecochain. 2021. Impact Categories (LCA) – Overview. [Online publication]. [Cited 2022-09-06]. Available: https://ecochain.com/knowledge/impact-categories-lca/

Ekholm, P. et al. 2020. Diffuse sources dominate the sulfate load into Finnish surface waters. Science of The Total Environment, vol. 748, p. 141297. ISSN: 0048-9697.

Elinkeinoelämän keskusliitto. 2022. Ulkomaankauppa. [Online publication]. [Cited 2022-10-05]. Available: https://ek.fi/tutkittua-tietoa/tietoa-suomen-taloudesta/ulkomaankauppa/

Fernandez, L. 2021. Global sulfuric acid market volume 2015-2026. Statista. Chemicals & Resources: Chemical Industry. [Online publication]. [Cited: 2022-05-16]. Available: https://www.statista.com/statistics/1245226/sulfuric-acid-market-volume-worldwide/

Fertilizers Europe. 2000. Best Available Techniques for Pollution Prevention and Control in the European Sulphuric and Fertilizer Industries. Booklet No. 3 of 8. Production of Sulphuric Acid. ESA. [PDF document]. Available: https://www.fertilizerseurope.com/wp-content/uploads/2019/08/Booklet_3_final.pdf

Focus on Catalysts. 2019. Global sulfuric acid market will reach $12.7 bn by 2024. Focus on Catalysts, vol. 2019, no. 4, pp. 2. ISBN: 1351-4180.

Gomes, R.M. & da Silva Junior, F.G. 2020. Impact of sulifdity on the kraft pulping of eucalyptus. BioResources, vol. 15, no. 2, pp. 3945-3961. ISBN: 3945-3961.

Gomez, D.R. et al. 2006. Chapter 2: Stationary Combustion. 2006 IPCC Guidelines for National Greenhouse Gas Inventories. [PDF Document]. Available: https://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/2_Volume2/V2_2_Ch2_Stationary_Combustion.pdf

Hajdu-Rahkama, R. & Puhakka, J.A. 2022. High tolerance of chemolithoautrophic sulphur oxidizing bacteria towards pulp and paper mill wastewaters and their organic constituents supporting sulphur recovery in alkaline conditions. Chemical Engineering Journal, vol. 450, p. 137972. DOI: https://doi.org/10.1016/j.cej.2022.137972

Hammerschmidt, J. & Wrobel, M. 2009. Decomposition of Metal Sulfates – A SO_2 -Source for Sulfuric Acid Production. Sulphur and Sulphuric Acid Conference. Outotec BmbH, Oberursel, Germany. The Southern African Institute of Mining and Metallurgy, pp. 87-100.

Hovikorpi, K.S. & Vakkilainen, E.K. 2019. Sources, collection, and handling of noncondensible gases in modern kraft pulp mills. TAPPI Journal, vol. 18, no. 5, pp. 297-305. ISBN: 0734-1415.

Hu, X. et al. 2020. Utilization of fly ash and wase lime from pulp and paper mills in the Argon Oxygen Decarbonization process. Journal of Cleaner Production, vol. 261, p. 121182. DOI: https://doi.org/10.1016/j.jclepro.2020.121182

Ilmatieteenlaitos. n.d. Rikkidioksidi. [Online publication]. [Cited 2022-05-10]. Available: https://www.ilmatieteenlaitos.fi/rikkidioksidi

Intang, K. et al. 2019. Life Cycle Assessment of Spent Sulfuric Acid from Lead-acid Traction Battery in Thailand. International Journal of Environmental Science and Development, vol. 10, no. 9, pp. 270-274. DOI: https://doi.org/10.18178/ijesd.2019.10.9.1186

Janssen, A.J.H. et al. 2009. Application of bacteria involved in the biological sulfur cycle for paper mill effluent purification. Science of The Total Environment, vol. 407. no. 4, pp. 1333-1343. DOI: https://doi.org/10.1016/j.scitotenv.2008.09.054

Jantunen, N. et al. 2019. Removal and recovery of arsenic from concentrated sulfuric acid by solvent extraction. Hydrometallurgy, vol. 187, pp. 101-112. ISSN: 0304-386X.

Jensen, A. et al. 2012. Methanol Purification System. PEERS Conference, pp. 2145-2176. [PDF document]. Available: http://www.ahlundberg.com/wp/wp-content/uploads/2017/05/AHL-Methanol-Purification-System.pdf

Justia. 2010. Process for directly producing sulfur trioxide and sulfuric acid using gypsum as raw material. [Online publication]. [Cited 2022-06-07]. Available: https://patents.justia.com/patent/8623319

Kekkonen, J. et al. 2013. Boliden Harjavalta Oy. Rikkihappotehtaan ympäristövaikutusten arviointiohjelma. Ramboll Finland Oy. [PDF document]. Available:

https://www.ymparisto.fi/download/noname/%7B2C50AD38-4DE7-428B-B62E-4DDFE4AD4BCD%7D/93793

Kekkonen, J. et al. 2014. Boliden Harjavalta Oy. Rikkihappotehtaan ympäristövaikutusten arviointiselostus. Ramboll Finland Oy. [PDF document]. Available: https://www.ymparisto.fi/download/noname/%7B1DE2DC67-7DB4-4E29-9606-A620BA414932%7D/99581

King, M.J. et al. 2013. Sulfuric Acid Manufacture: Analysis, Control and Optimization (2nd Edition). Elsevier. 493 pp. ISBN: 978-0-08-098220-5.

KnowPulp. n.d. [Online learning environment]. [Cited 2022-05-03]. Available: https://www-knowpulp-com.ezproxy.cc.lut.fi/extranet/knowpulp.htm

LabChem. 2020. Sodium Hydroxide, 20 % w/v – Safety Data Sheet, version 1.2. Federal Register. Rules and Regulations, vol. 77, no. 58, pp. 9. [PDF document]. Available: http://www.labchem.com/tools/msds/msds/LC24090.pdf

Laursen, J.K. & Karavanov, A.N. 2006. Processess for sulfur recovery, regeneration of spent acid, and reduction of NOx emissions. Chemical and Petroleum Engineering, vol. 42, no. 5, pp. 229-234. DOI: https://doi-org.ezproxy.cc.lut.fi/10.1007/s10556-006-0084-3

Likus-Cieslik, J. et al. 2017. Spatial distribution and concentration of sulfur in relation to vegetation cover and soil properties on a reclaimed sulfur mine site. Environmental monitoring and assessment, vol. 189, no. 2, p. 87, pp. 1-12. DOI: https://doi-org.ezproxy.cc.lut.fi/10.1007/s10661-017-5803-z

Mahecha-Botero, A. et al. 2021. Concentrated sulfuric acid production from non-condensable gases and its effect on alkali and sulfur balances in pulp mills. Nordic Pulp & Paper

Research Journal, vol. 36, no. 1, pp. 100-107. DOI: https://doi-org.ezproxy.cc.lut.fi/10.1515/npprj-2020-0049

MarineFinland. 2020. There is only a little salt in the waters of the Baltic Sea. [Online publication]. [Cited 2022-11-21]. Available: https://www.marinefinland.fi/en-US/The_Baltic_Sea_now/Water_quality/Salinity

Martin, R. 2014. 10 major industrial application of sulfuric acid. [Online publication]. [Cited 2022-05-13]. Available: https://www.slideshare.net/bejoybj/10-major-industrial-applications-of-sulfuric-acid#

Marwa, M. et al. 2017. An Environmental Life Cycle Assessment of an Industrial System: Case of Industrial Sulfuric Acid. International Journal of Energy, Environmental, and Economics, vol. 25, no. 4, pp. 255-268. ISSN: 1054-853X.

Maslin, M. et al. 2022. Sulfur: A potential resource crisis that could stifle green technology and threaten food security as the world decarbonises. The Geographical Journal, vol. 00, pp. 1-8. DOI: https://doi.org/10.1111/geoj.12475

McLean, S. H. et al. 2022. A case study comparison of a sulphuric acid plant with and without on-site low-grade heat recovery and repurposing. The International Journal of Life Cycle Assessment, vol. 27, pp. 655-664. DOI: https://doi-org.ezproxy.cc.lut.fi/10.1007/s11367-022-02052-x

Metsäteollisuus. 2022. Metsäteollisuuden tuotanto kasvoi viime vuonna. [Online publication]. [Cited 2022-10-25]. Available: https://www.metsateollisuus.fi/uutishuone/metsateollisuuden-tuotanto-kasvoi-viime-vuonna

Mäki, E. et al. 2021. Drivers and barriers in retrofitting pulp and paper industry with bioenergy for more efficient production of liquid, solid and gaseous biofuels: A review. Biomass and Bioenergy, vol. 148, p. 106036. https://doi.org/10.1016/j.biombioe.2021.106036

Nleya, Y. et al. 2016. Sustainability assessment of the recovery and utilization of acid from acid mine drainage. Journal of Cleaner Production, vol. 113, pp. 17-27. ISBN: 0959-6526.

Persson, L. et al. 2022. Outside the Safe Operating Space of the Planetary Boundary for Novel Entities. Environmental Science & Technology, vol. 56, pp. 1510-1521. DOI: https://doi.org/10.1021/acs.est.1c04158

Pio, D.T. et al. 2022. Carbon neutral methanol from pulp mills towards full energy decarbonization: an inside perspective and critical review. Green Chemistry, vol. 24, no. 14, pp. 5403-5428. DOI: https://doi-org.ezproxy.cc.lut.fi/10.1039/D2GC01528E

Polowski, N.V. et al. 2006. A Kinetic Mathematical Model of Kraft Pulping Process for Control and Optimization Applications. IFAC Proceeding Volumes, vol. 39, no. 2, pp. 291-295. ISBN: 9783902661036.

Pöyry. 2018. Ympäristövaikutusten arviointiohjelma. Stora Enso Oyj: Oulun tehtaan tuotantosuunnan muutos, pp. 113. [PDF document]. Available: https://www.ymparisto.fi/download/noname/%7B873BD1CE-8FB1-4410-BD2A-81CEC98D7DCE%7D/138498

Quansys Biosciences. 2022. Dilutions: Explanations and Examples of Common Methods. [Online publication]. [Cited 2022-09-06]. Available: https://www.quansysbio.com/support/dilutions-explanations-and-examples/

Rockström, J. et al. 2009. Planetary Boundaries: Exploring the Safe Operating Space for Humanity. Ecology and Society, vol. 14, no. 2, pp.1-33.

Runkel, M. & Sturm, P. 2009. Pyrite Roasting, an Alternative to Sulphuric Burning. Sulphur and Sulphuric Acid Conference. Outotec BmbH, Oberursel, Germany. The Southern African Institute of Mining and Metallurgy, pp. 101-110.

Rypdal, K. et al. 2006. Chapter 1: Introduction to the 2006 Guidelines. 2006 IPCC Guidelines for National Greenhouse Gas Inventories. [PDF Document]. Available: https://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/1_Volume1/V1_1_Ch1_Introduction.pdf

Satein, H. 2009. Chemical Relationships between Greenhouse Gases and Air Pollutants in Biomass Energy Production. Oregon Toxics Alliance. [PDF document]. Available: https://www.beyondtoxics.org/wp-content/uploads/2011/11/OTA_Report-BiomassContributors_to_ClimateChange7-28-09.pdf

Schlesinger, M.E. et al. 2011. Capture and Fixation of Sulfur. In book: Schlesinger, M.E. et al. Extractive Metallurgy of Copper. Elsevier. ISBN: 978-0-08-096789-9

SFS-EN ISO 14040: 2006. Environmental management. Life cycle assessment. Principles and framework. Finnish Standards Association SFS.

SFS-EN ISO 14044: 2006. Environmental management. Life cycle assessment. Requirements and guidelines. Finnish Standards Association SFS.

Song, K. et al. 2013. Recovery of high purity sulfuric acid from the waste acid in toluene nitration process by rectification. Chemosphere, vol. 90, no. 4, pp. 1558-1562. ISSN: 0045-6535.

Sphera. 2020. Beverage Packaging Life Cycle Assessment. Graphic Packaging International. [PDF document]. Available: https://www.graphicpkg.com/documents/2020/11/life-cycle-assessment-2020.pdf/

Sphera. n.d. Environmental Footprint (EF)/ILCD recommendation. [Online publication]. [Cited 2022-10-14]. Available: https://gabi.sphera.com/international/support/gabi/gabi-lcia-documentation/environmental-footprint-efilcd-recommendation/

Steffen, W. et al. 2015. Planetary boundaries: Guiding human development on a changing planet. Science, vol. 347, no. 6223, pp. 736-746. DOI: https://doi.org/10.1126/science.1259855

Suhr, M. et al. 2015. Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper and Board. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). JRC Science and Policy Reports. [PDF document]. Available: https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/PP_revised_BREF_2015.pdf

Sulphuric Acid on the Web. 2006. Sulphur Systems – Sulphur Filtration. [Online publication]. [Cited 2022-07-12]. Available: http://www.sulphuric-acid.com/techmanual/sulphur/filtration.htm

SYKE. 2018. Finland and sustainable well-being: Planetary boundaries already partly overstepped. [Online publication]. [Updated 2018-09-14]. [Cited 2022-05-10]. Available:

https://www.syke.fi/en-US/Finland_and_sustainable_wellbeing/Planetary_boundaries_need_to_be_considered/Planetary_boundaries_already_partly_over(47931)

SYKE. 2020a. Ilman epäpuhtauksien päästöt Suomessa. [Online publication]. [Updated 2022-03-24]. [Cited 2022-05-10]. Available: https://www.ymparisto.fi/fi-fi/kartat_ja_tilastot/ilman_epapuhtauksien_paastot

SYKE. 2020b. Sulfaattikuormitus voi vaarantaa vesistöt. [Online publication]. [Cited 2022-05-10]. Available: https://www.syke.fi/fi-FI/Ajankohtaista/Sulfaattikuormitus_voi_vaarantaa_vesisto(58407)

Umweltbundesamt. 2017. Sulphuric Acid Production. Environment Agency Austria. Vienna. [PDF document]. Available: https://www.umweltbundesamt.at/fileadmin/site/themen/industrie/sulphuric_acid_production-installation_3-5.pdf

USEPA. 2022. Acid Plant New Source Review Enforcement Initiative. [Online publication]. [Cited 2022-09-02]. Available: https://www.epa.gov/enforcement/acid-plant-new-source-review-enforcement-initiative

Valmet. 2016. Valmet to supply a sulfuric acid plant to the Metsä Group bioproduct mill in Äänekoski, Finland. [Online publication]. [Cited: 2022-06-02]. Available: https://www.valmet.com/media/news/press-releases/2016/valmet-to-supply-a-sulfuric-acid-plant-to-the-metsa-group-bioproduct-mill-in-aanekoski-finland/

Valmet. 2017. Control of sulfidity in a modern kraft pulp mill. Valmet Technical Paper Series. [PDF Document]. Available: https://www.valmet.com/globalassets/media/downloads/white-papers/power-and-recovery/controlling_sulfidity_whitepaper.pdf

Valmet. 2022. Valmet Methanol Purification – Unleashing the green value of methanol. [Online publication]. [Cited 2022-10-19]. Available: https://www.valmet.com/media/articles/pulping-and-fiber/unleashing-the-green-value-of-methanol/

Wagenfeld, JG. et al. 2019. Sustainable applications utilizing sulfur, a by-product from oil and gas industry: A state-of-the-art review. Waste Management, vol. 95, pp. 78-89. ISSN: 0956-053X.

Wahoud, A. et al. 2011. Sulfuric acid baking and leaching of spent sulfuric acid catalyst. Periodica Polytechnica. Chemical Engineering, vol. 55, no. 1, pp. 31-34. DOI: https://doi.org/10.3311/pp.ch.2011-1.06

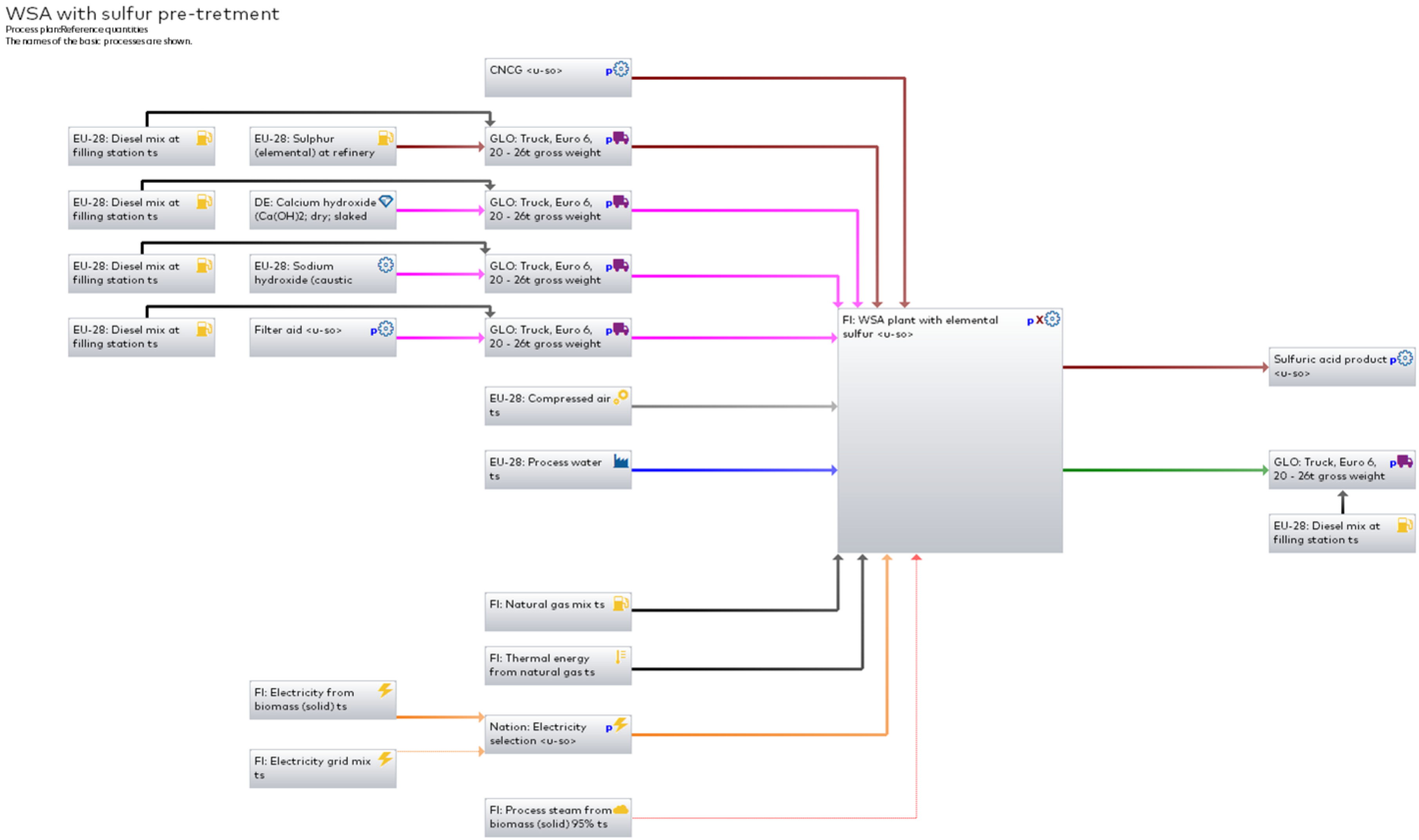
Wang-Erlandsson, L. et al. 2022. A planetary boundary for green water. Nature Reviews Earth & Environment, vol. 3, pp. 380-392. DOI: https://doi.org/10.1038/s43017-022-00287-8

Williams, M. & Minjares, R. 2016. A technical summary of Euro 6/VI vehicle emission standards. ICCT. [PDF document]. Available: https://theicct.org/sites/default/files/publications/ICCT_Euro6-VI_briefing_jun2016.pdf

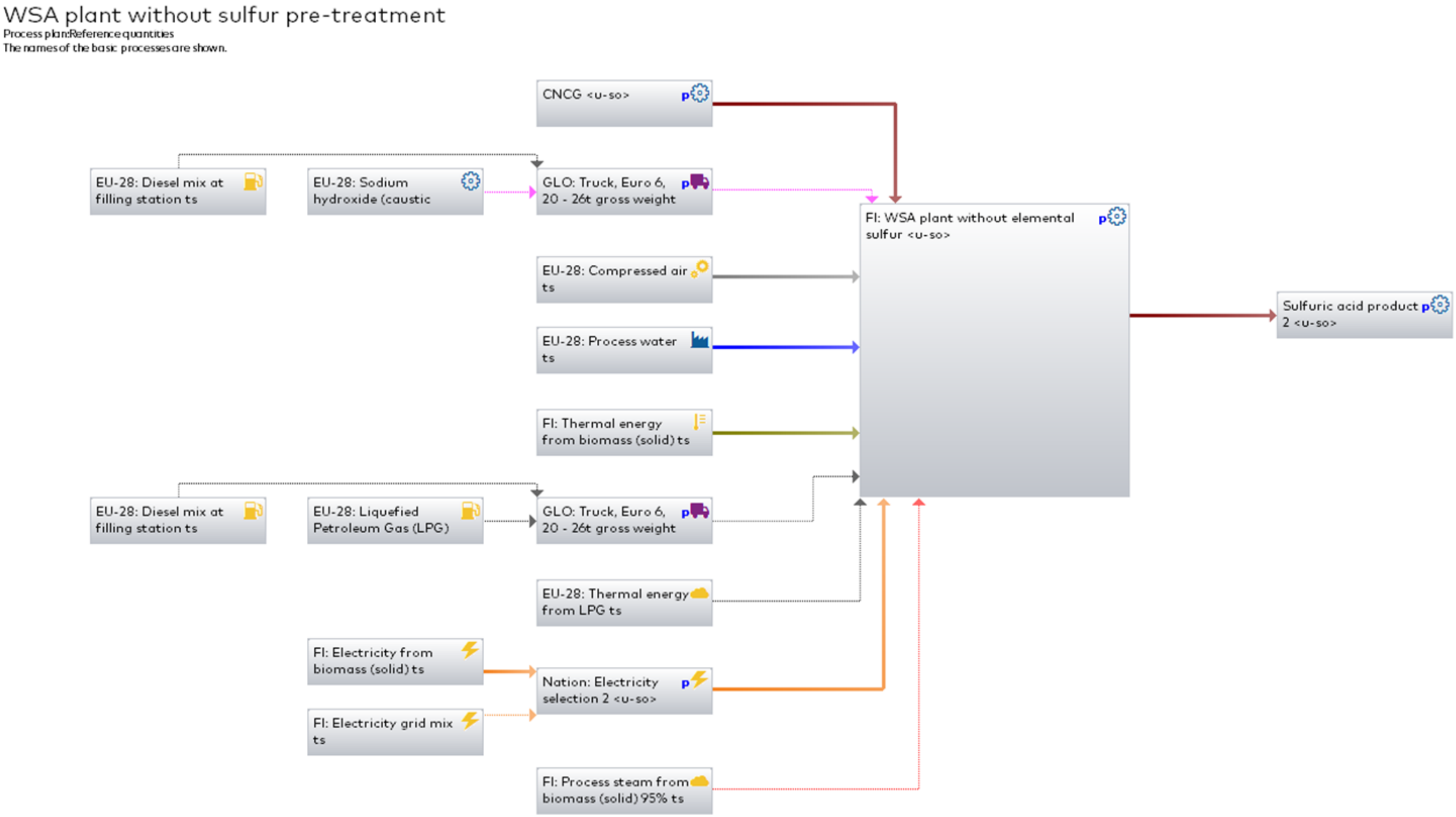
Wu, S. et al. 2020. Co-preparation of calcium sulfoaluminate cement and sulfuric acid through mass utilization of industrial gypsum. Journal of Cleaner Production, vol. 265, p. 121801. ISSN: 0959-6526.

Wulca. n.d. FAQ: What are the units and what do they mean? [Online publication]. [Cited 2022-10-14]. Available: https://wulca-waterlca.org/aware/faq/

Appendix 1: Figure of the GaBi model for the process with elemental sulfur.



Appendix 2: Figure of the GaBi model for the process without elemental sulfur.



Appendix 3: GaBi processes of the model for the process with elemental sulfur.

Processes	**Last updated**
EU-28: Sulphur (elemental) at refinery	1.1.2020
DE: Calcium hydroxide (Ca(OH)2; dry; slaked lime) (EN15804 A1-A3)	1.1.2020
EU-28: Sodium hydroxide (caustic soda) mix 100 %	1.1.2020
EU-28: Compressed air (10 bar, high efficiency)	1.1.2020
EU-28: Process water (ion exchange, surface water)	1.1.2020
FI: Natural gas mix	1.1.2020
FI: Thermal energy from natural gas	1.1.2020
FI: Electricity from biomass (solid)	1.1.2020
FI: Electricity grid mix	1.1.2020
FI: Process steam from biomass (solid) 95 %	1.1.2020
GLO: Truck, Euro 6, 20-26t gross weight / 17.3t payload capacity	1.1.2020
EU-28: Diesel mix at filling station	1.1.2020

Appendix 4: GaBi processes of the model for the process without elemental sulfur.

Process	**Last updated**
EU-28: Sodium hydroxide (caustic soda) mix 100 %	1.1.2020
EU-28: Compressed air (10 bar, high efficiency)	1.1.2020
EU-28: Process water (ion exchange, surface water)	1.1.2020
EU-28: Liquefied Petroleum Gas (LPG) (70 % propane, 30 % butane)	1.1.2020
EU-28: Thermal energy from LPG	1.1.2020
FI: Thermal energy from biomass (solid)	1.1.2020
FI: Electricity from biomass (solid)	1.1.2020
FI: Electricity grid mix	1.1.2020
FI: Process steam from biomass (solid) 95 %	1.1.2020
GLO: Truck, Euro 6, 20-26t gross weight / 17.3t payload capacity	1.1.2020
EU-28: Diesel mix at filling station	1.1.2020