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Cover: A picture of bark from a debarker

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Abstract

This review is written to compile most of the studies done in the field of pyrolysis of bark. It is directed towards the forest industry and companies producing chemical components. The results of this review are meant to be an introduction to pyrolysis of bark as a mean to produce a valuable raw material. Bark is a waste product in the forest industry. Since the price of oil is rising and the interest towards sustainable alternatives also is on the rise, this process and usage of wood waste could be a viable alternative to oil based feedstocks. Bark has favourable properties energy-wise as well as chemically. Therefore it is suitable, after upgrading, as a feedstock in the industry for production of chemical components. However, more research and experiments need to be done in the field. The process of pyrolysis of bark is to a great extent not applicable in an industrial scale with present technology.

Keywords: Pyrolysis; Biomass; Bark; Sustainable; Wood waste

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Introduction

This study is partially a continuation of a previous project, which examined renewable raw materials aimed at the plastic industry. Borealis, a petrochemical industry that produces plastic products from petroleum, has shown interest towards environmentally friendly raw materials. They support this project in collaboration with Holmens Skog, a company in the Swedish forest industry branch. The previous project was a broad study of new raw materials from the forest industry. Pyrolysis was one of the methods that showed a potential to be viable [1].

Borealis is a company that produces polyolefines, base chemicals and fertilisers. The site in question for this study is the Stenungsund site, which primarily produces polyolefins but also base chemicals. This study is aimed at the evaluation of pyrolysis of bark as a method to produce ethylene that is an important raw material for the site.

Holmen is a large forest owner and a producer of paper and other wood products. The site in question for this study is the Iggesund site, which produces paperboard, printing paper and sawn timber. The aim of this study is to evaluate how the bark, a wood waste product, could be used to create a product of higher value than just use it for heat production through combustion, which is its current use.

Due to the large forest industry in Sweden and the other Nordic countries the range of raw materials has been limited to forest products in this project. The waste products of the industry have been more interesting due to the economic aspects of potential products. In this review bark has been chosen since it is a wood waste mostly used for energy production through combustion although it has an interesting chemical composition, usable for other purposes [2].

This study will cover the chemistry and composition of bark. Pine bark from Scots pine, *Pinus Sylvestris*, and Norwegian spruce, *Picea Abies*, have been chosen since they are the most common bark types in the Swedish forest industry. Some of the data has been collected at the Iggesund site, a paper mill and sawmill owned by Holmen. However, most of the data on pine bark before processing originate from the organisation Värmeforsk. Värmeforsk is a Swedish organisation that conducts research and development dealing with energy and forestry. When searching for data on bark, the main concern has been to find detailed enough results. Only few studies have looked specifically at bark. Bark was usually only treated while researching other or broader perspectives of something, for example when studying other wastes or alongside wood.

Bark used as a material in pyrolysis is presented by a walkthrough of the process. Products, by-products and wastes will be covered as well as some sample means of pyrolysis and separation. Due to extensive use of the fluidised bed reactors in pyrolysis research and the poor focus on

bark, the presented data is focused on the fluidised bed pyrolysis method. Since solids are one of the unwanted products of pyrolysis, some separation methods will be suggested.

A few of the questions used as search terms have been “Pyrolysis of wood waste”, “Pyrolysis of bark”, “Properties of bark” and “Chemistry of bark”. An important search term due to bark’s differences from other, more researched biomasses, has been “Pre-treatment of bark towards pyrolysis”.

Problem

This report aims to answer the following questions. This is a complement to the broader study with the details concerning pyrolysis of bark.

- Can bark be used as raw material when producing hydrocarbons?
- Is pyrolysis a viable method when using bark as a raw material?

Method

The method used throughout this study has been to search in journals and databases for relevant material using keywords or phrases. Chalmers Library search functions and consultation from professors and researchers have been used. The retrieved information was compiled and structured in this paper.

Scope

The aim of this paper is to study bark as a raw material when using pyrolysis. Products, by-products and properties of bark will be discussed. The main focus will be to describe the chemistry and properties of bark and then the process and the properties of the products when using bark as a raw material in the pyrolysis process. A more detailed study of the methods of pyrolysis, pre-treatment and separation are not dealt with due to the fact that these areas have already been covered in other studies.

Introduction to Pyrolysis

Pyrolysis has been used in the Nordic countries for centuries in the production of pine tar and charcoal. The production process took several days. It was an important industry until the 20th century, when the practise more or less ceased since ships started to be built of metal and the overall usage of tar plummeted. The shipyards did not use tar anymore. In later years pyrolysis has been revived as a viable method to produce biofuels and chemical components.

The modern practise is radically different from the historical one. Efficiency and desired products differ, and hence the process has been altered to match modern demands. Today, volatiles and oils are the desired products and not the solids. Consequently, the processes involved demand shorter reaction times and higher temperatures. The resulting bio-oil can be utilised in the production of fuels as well as chemical components.

The largest industrial use of pyrolysis is within the food industry. The production of food additives, flavour and colouring, are the main products of the practise. The main method used in this industry is

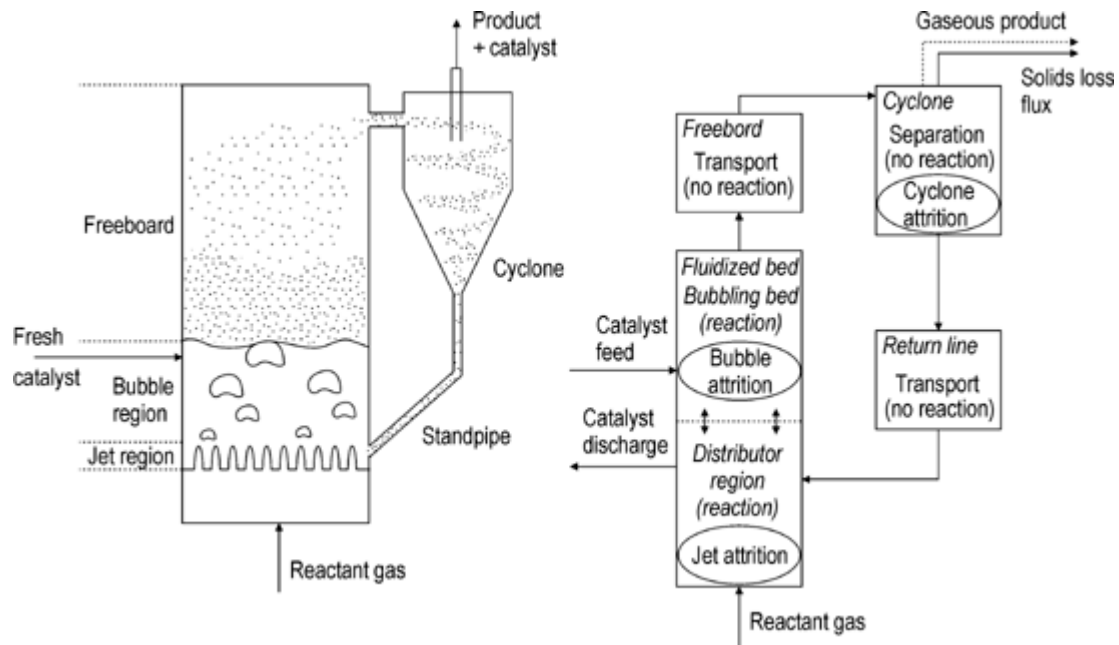


Figure 1: Fluidised bed reactor [20]

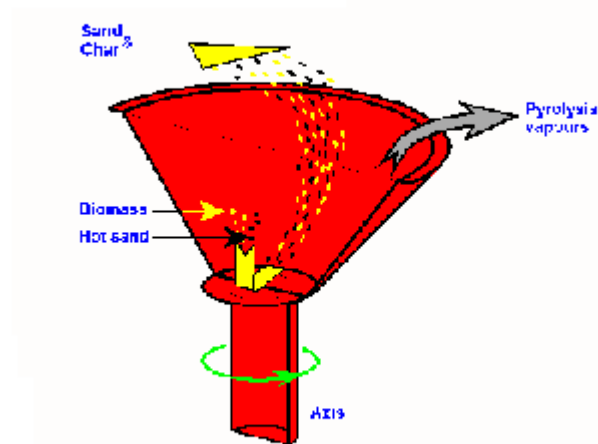
the fluidised bed reactor. The fluidised bed reactor is a reactor type in which sand and biomass are held in suspension by a hot gas. The reactor itself and the sand are heated and the heat transfer is taken place through the sand and the reactor walls. The sand and char are then separated through a vortex. The sand is then re-circulated.

The process will always produce three product phases: Solid, liquid and gas. One can tune the process to favour one of the phases but it is not possible to completely eliminate the other phases. This leads to the need for a separation process downstream from the reactor. A common way to remove the solid phase, char and minerals, is cyclone separation. Selective condensation is used to remove the unwanted gas phase consisting of non-condensable organics, carbon oxides and nitrous oxides, leaving the remaining wanted liquid phase.

The three pyrolysis reactor types treated in this study are the fluidised bed reactor, the auger reactor and the ablative vortex reactor. As previously stated, the fluidised bed reactor is the most common and a relatively well researched method of pyrolysis [3]. The basics of the process is to feed the biomass particles into the reactor together with heated sand, which is inert, and use an inert flue gas that is heated. The stream is then separated by the common pyrolysis separators, with the difference that the sand and flue gas are recirculated.

The ablative vortex reactor is treated in this study only because of its potential and the fact that it is not very well researched, although it could very well be the most effective method of pyrolysis. The basic

Figure 4—Rotating cone pyrolysis reactor.



Source: Prins, W. and BM. Wagenaar, 1997. In Biomass Gasification and Pyrolysis. Eds. Kalschmitt, MK and AV. Bridgwater, pp 316-326. (CPL Press)

Figure 2: Ablative vortex reactor [21]

process of the ablative vortex reactor is to feed the biomass, with or without heated sand, into a funnel shaped, rotating, and heated reactor vessel [4]. The principle that differs the ablative reactor from other reactors is that the heat transfer mainly takes place through the walls of the reactor rather than through a medium [5]. Because of the superior method of heat transfer, larger biomass particles can be more effectively handled in the ablative vortex reactor compared to other reactors.

The auger reactor is in part a kind of ablative reactor although it has a flute gas that acts as a heat transfer medium [6]. It has a heated screw that works for both heat transfer and the mechanical movement of the biomass. Otherwise the setup is more or less similar to the methods previously described for pyrolysis as the products are the same [7].

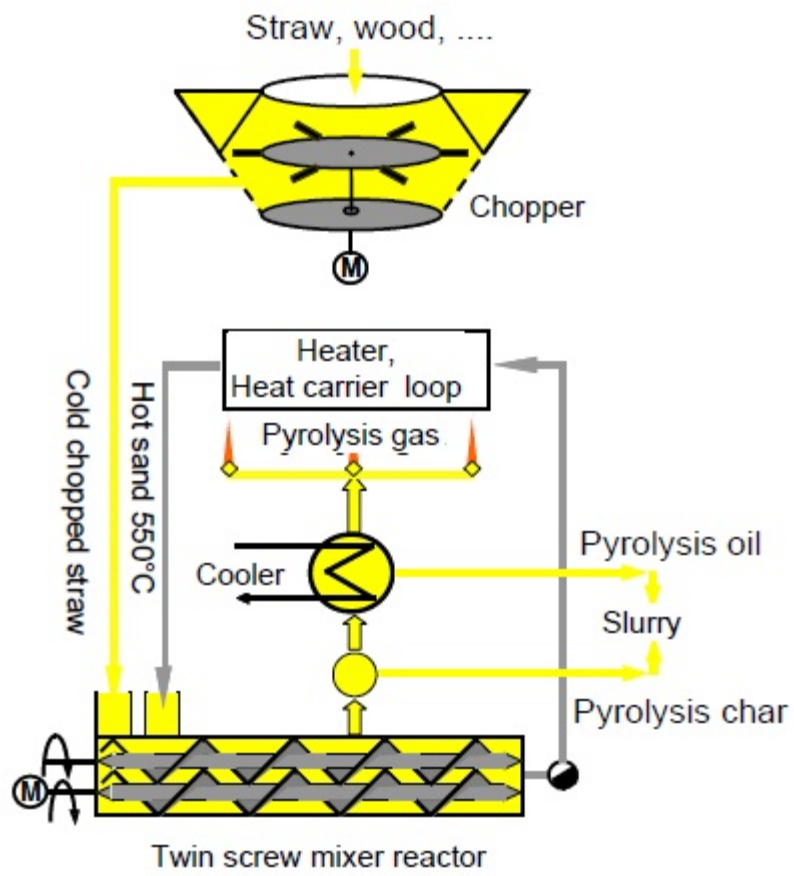


Figure 3: Twin screw Auger reactor [22]

Properties and Composition of Bark

Bark is a by-product in all forest industries, with the exception of a pellet factory in Mönsterås, owned by Södra [8], a Swedish forest cooperative that produces paper and other refined wood products. Otherwise bark is mainly used as a fuel for heating purposes. However, due to the usually high water content, the distinction between combustion and destruction is vague. When considering bark as a fuel, the heating value when dry is ~21.5 MJ/kg for the common Nordic softwoods. This can be compared to the heating value when wet, which is 8.8 MJ/kg. The economic value of bark is SEK 130/MWh at <60 wt% water content. The amount produced every year is ~3.6 M ton. 82 % of the bark is from softwoods, more precisely *Pinus Sylvestris* and *Picea Abies* as seen in Fig.1. The elemental composition of pine bark can be seen in Table 1.

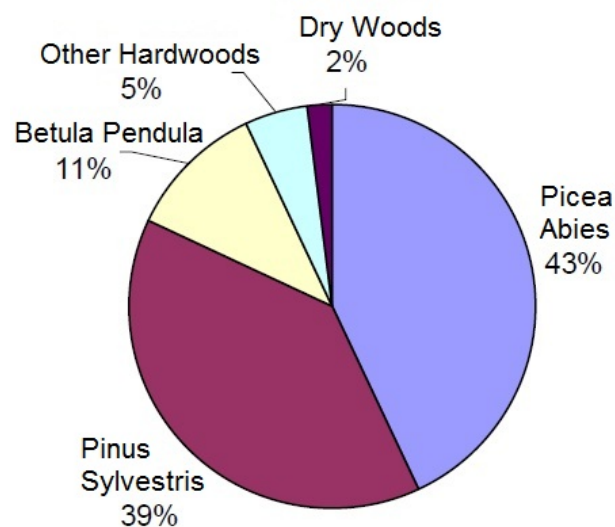


Figure 4: Types of bark common in Sweden [9]

Table 1: Composition of pine bark [10]

Element	C	H	N	S	O
Composition of pine bark	55,9	5,3	0,4	0,02	37,1

A difficulty when using bark as a fuel by means of combustion is the physical size of the bark after debarking of the logs. Empirical studies have shown that the bark can be separated into a fine and a coarse fraction. The fraction distribution from a common debarker of barrel type, of which the larger fractions are processed through a grinder, can be seen in Table 2. It is interesting that the fine fraction (<2mm) is highly unwanted in a furnace, due to coking, while it is ideal in a pyrolysis process. In a furnace the small fraction will increase the soot content and create an isolating layer inside the furnace as well as increased maintenance needs. The debarking process that produces the largest quantity of the fine fraction is that at a pulp mill. Since bark is an unwanted product in the forest industry there is a

great potential to optimise the pyrolysis process to extract the desired products. The inorganic composition of the slightly larger fraction 0,250-0,450mm is shown in *Table 3*.

Table 2: Bark fractions in order of size [11]

Fraction size (mm)	x>91,5	91,5>x>50	50>x>31,5	31,5>x>16	16>x>8	8>x>4	4>x>2	2>x
Partition (%)	1,5	4,9	2,3	4,4	14,4	20,8	21,2	30,4

Table 3: Inorganic composition of bark in the 0,250-0,450 mm fraction range [12]

	Picea Abies	Pinus Sylvestris
N(%)	0,49	0,48
Ca(%)	0,439	0,374
Mg(%)	0,079	0,06
Na(%)	0,014	0,01
K(%)	0,242	0,175
P(%)	0,14	0,194
Cu(mg/kg)	3,68	2,12
Zn(mg/kg)	145,87	38,74
Ni(mg/kg)	3,69	3,2
Cr(mg/kg)	1,46	6,59
Pb(mg/kg)	2,11	1,56

When using bark as a raw material, ashes and minerals will be a large part of the formed or remaining solids. The amount of ash varies greatly, between 1,5 %-6 %, and this has an impact on the concentration of minerals and salts in the solid phase. This is particularly interesting since it has consequences downstream from the pyrolysis reactor. Solids need to be removed from the product stream or they may poison the catalysts downstream. Depending on the composition of the solids, they may be very challenging for the separation units and/or the reactor. In *Table 4* some results are presented for ash and dry matter from the Holmen site in Iggesund. The samples are taken at three different times during one day.

Table 4: Dry matter and ashes, achieved through combustion

Iggesund	Dry matter [wt%]	Ashes [wt%]
Morning	41	2,8
Noon	36,4	2,9
Evening	43,2	3,02

Bark as raw material for fast pyrolysis

This chapter presents a walkthrough of the key steps in fast pyrolysis process when using bark as raw material.

1. Raw material and Pre-treatment

Bark is produced in large quantities by the paper and forest industry. One of the early steps in the paper industry process is to completely remove the bark from the logs through debarking. In today's paper mills the bark is collected and burned as an energy source. The heating value of the bark at this stage is low due to the high water content, which is usually around 50 wt%.

To use bark as a biomass in pyrolysis towards bio-oil, especially where saturated hydrocarbons are desired, the high water content is problematic. Drying the biomass is necessary. This can be done in different ways, but active drying is needed if bark is to be used at an industrial scale. For optimal pyrolysis the water content must be <10 wt% and ideally 0 wt%.

The physical size and structure of the bark from the paper industry varies from very small particles to ~100 mm chunks, see table 2. Regardless of the method of pyrolysis, grinding is needed to create a usable biomass. Different methods tolerate different particle sizes. The largest particle size tolerated by the methods in this study is <4 mm [13].

2. Fast Pyrolysis

One of the largest problems in fast pyrolysis of biomass is heat transfer. In the pyrolytic reaction, oils, tar and char will deposit on the surface of the biomass particles. The deposited materials reduce the heat transfer and must be removed. In the fluidized bed reactor the sand will scrape off the unwanted coating through the abrasive effect of the moving sand within the reactor. The sand and flue gas also act as media for heat transfer. In the ablative reactor the coating is removed through contact and friction against the reactor walls [14].

Depending on the desired composition of the product stream, residence time and temperature will be the determining factors. High temperature and short residence time favour more liquid yield and fewer solids. Experiments have been performed with yields up to 75 % liquids according to Bridgwater [4]. A simplified orientation of the correlation between temperature, residence time and product type, can be seen in *Table 5*.

Table 5: Residence time, temperature and products of pyrolysis (wood) [4]

Mode	Conditions	Liquid	Solid	Gas
Fast	~500°C, short hot vapour residence time ~1s	75%	12% char	13%
Intermediate	~500°C, hot vapour residence time ~10-30s	50% in 2 phases	25% char	25%
Carbonisation (slow)	~400°C, long vapour residence time days	30%	35% char	35%
Gasification	~750-900°C	5%	10% char	85%
Torrefaction (slow)	~290°C, solids residence time ~10-60min	0% unless condensed, then up to 5%	80% solid	20%

An Auger reactor works very similar to a fluidised bed reactor. It utilises sand as a heat transfer medium but the biomass and sand are mixed mechanically with a screw instead of through interaction with a flute gas. Some data on the pyrolysis of bark in a bench-scale Auger reactor can be seen in *Table 6*.

Table 6: Water content, pH, Density and Solids from bench-scale Auger reactor [15]

	Water content wt%	pH/water	Density g/cc	Solids %
Pine Bark	19,8	3,2	1,17	2,1

The ablative vortex reactor type is not researched as well as the fluidised bed reactor, but there are some results available. The direct heat transfer gives slightly different results and the water production differs [16]. The reactor can be utilised with or without sand as an additional heat transfer medium.

The fluidised bed reactor has the most detailed data collected to date. The main compounds and the phase compositions are presented in *Table 7*.

Table 7: Composition of pyrolysis products from an experimental fluidised bed reactor [17]

Main Compounds %		Compounds in aqueous phase mg/l		Gas products mol%	
Phenols	51,61	Hydroxymethylfurfural	653,6	Methane	11,84
Ketones	9,32	Furfural	3040,2	Ethane	1,62
Aldehydes	14,12	Methylfurfural	268,4	Ethylene	0,89
Aromatic Compounds	1,23	Glycolaldehyde	8693	Propane	0,37
Carboxylic Acids	3,16	Hydroxyacetic Acid	2433	CO ₂	45,89
Esters	1,76	Formic Acid	680,3	CO	30,48
		Acetic Acid	35826	H ₂	3,87
		Total Phenol	10,9	Others	5,05
		Water wt%	82,8		

3. Separation and Purification

Since the process will result in a non-condensable phase, a condensable phase and a solid phase, the first separation steps will always look the same, regardless of process. It is always necessary to remove the solid phase; this is usually done with a cyclone unit. The solid phase is mainly char, minerals and sand, if sand is used in the reactor. It is very important that the stream is completely free from solids if the product stream is to be upgraded, which here means removing water and reducing oxygen content. Bark shows a high mineral content which leads to more solids than wood.

Today the mechanics of pyrolysis is fairly unknown. There are hundreds of parallel reactions that make the whole process extremely complex. Empirical studies show, after the controlled pyrolysis inside the reactor has taken place, that the product stream needs to be cooled down to a temperature of <50 °C to stop the reactions. The non-condensable and condensable phases will otherwise continue the reaction towards tar and coal.

4. Upgrading the bio-oil

The product stream, regardless of method, has to be upgraded to be viable as a feed for a cracker. Oxidised hydrocarbons are not wanted in the feed since this will lead to a higher degree of coking of the cracker. Water is also a highly unwanted component in the pyrolysis product stream. However, as stated by Bridgwater, as a rule of thumb there will be roughly 15 wt% water content produced during the pyrolysis. Hence, there will always be an unwanted water phase to be either removed or upgraded.

Some of the water-soluble polar components, such as alcohols, are upgradeable but there will still be some water content that has to be removed. One method of removing water that has been studied is the use of zeolites. This should also be combined with oxygen removal since many of the physical properties of the bio-oil are dependent on the presence of water, such as pH, viscosity and stability. Oxygen can be removed by a catalytic reaction in the presence of hydrogen. The resulting water can be removed through application of zeolites [17][18].

As of today there are two different ways to upgrade crude bio-oil. Both are catalytic but one is based on cracking and the other on hydrotreating. The most common problem with upgrading is to achieve an acceptable efficiency. This problem is due to coking of the catalyst [19].

Discussion

It should be noted that both drying and grinding are very energy-consuming steps; therefore large particles are acceptable as well as some water content. The energy invested in grinding and drying has to be compared to the energy saved downstream. However, these both steps are needed when utilising pyrolysis using wood or other kinds of biomass. They should therefore not be considered as difficulties when comparing various types of biomass as raw material for pyrolysis processes. Water is always unwanted due to its oxidising effect and energy consumption, but unavoidable due to the nature of biomass.

A problem when looking at the process of pyrolysis using bark compared to wood is the highly varying, but usually high, amount of ashes. This could prove to be a problem depending on the pyrolysis method. It will be a problem during the separation of the wanted phase, increasing the amount of minerals and other solids in the product stream. Using bark as a raw material in a pyrolysis process is more demanding when considering separation and after-treatment of the product stream.

Among the chosen methods of pyrolysis, the ablative vortex is unfortunately the least researched method. However, it could very well be the method of choice if tried and optimised. It is the only method with nothing more than the biomass within the reactor. This, of course, simplifies the downstream separation of the various components in the product stream from the reactor. Hopefully the non-condensable gases from the process could be used as a propellant and heat source in the process. This, of course, needs further study and experiments. One of the largest difficulties with the ablative vortex reactor is to heat the metal walls of the reactor. Another problem identified in bench-scale testing was that some nanoparticles of coal may form and be carried by the gas-phase and mix with the product.

Upgrading is necessary if the bio-oil is to be used in petrochemical production or even as a fuel. Since most hydrocarbons created in the pyrolysis are oxidised, there has to be an upgrading step removing the oxygen. This is needed whatever method of pyrolysis that is in use. For example, in the process of cracking one has to consider a certain oxygen content. The presence of oxygen in the cracker tower gives the highly unwanted effect of coking that creates a much higher need for maintenance. A cracker tower needs to run continuously for several years to optimise economic efficiency, which makes additional coking a critical problem.

Conclusions

Bark is, without question, a potential raw material for pyrolysis. Considering the current economic value of bark in the forest industry, the most likely scenario would be that the pyrolysis plant is located at a paper mill. Paper mills have their own production of heat that may or may not be distributed to adjacent communities. That excess production of heat could easily be utilised in the drying process. Since the bark is separated from the wood at the site, there will also be an economical gain concerning less transportation needs.

Other aspects, such as grinding, are also better if the production is located at a paper mill. The separation of bark from wood can be optimised with a focus towards pyrolysis to save energy in the grinding step. To some extent the same or similar equipment that is used in the pre-treatment of wood at a paper mill could be utilised. This in turn will make maintenance of grinders, and such, easier.

A hydrogen stream is needed for the process. Stenungsund has one that is suitable; a paper mill lacks such a facility. When removing water and oxygen from the bio-oil a hydrogen stream is needed. To create a hydrogen stream at a paper mill is not economically defensible. Thus the upgrading of the bio-oil is best done closer to its end user, such as in the chemical industry.

Future Work

The largest difficulty performing this study has been the meagre availability of previous studies on the subject. There are several studies on pyrolysis of wood, other biomasses and bio-oil, but there is a need for more studies focused on pyrolysis of bark. There has yet to be a thorough study on the pyrolysis of pine bark. Pyrolysis of bark is a subject that needs much more attention considering the value of bark as a raw material and the handling of bark in today's forest industry. The heating value is more or less negligible and hence studies that suggest methods that create a higher economic value, are interesting.

Empirical studies of bark as a raw material in various methods of pyrolysis, such as ablative vortex and variations of fluidised bed, are desired. Most studies have only discussed bark while focusing on wood or other organic matters. It would be beneficial if more studies focusing on bark and its properties were done. A large study on the resulting bio-oil and its composition is not only wanted, but could also be the first part of a study on the upgrading processes and applications of bio-oil.

Overall there is much to be done on the subject, but the potential of bark as a secondary source of income for the forest industry is undeniable.

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