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Biomass based energy intermediates boosting biofuel production

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Deliverable 5.11
Process flow diagram and description of the phenol recovery process from pyrolysis oil and economic exploitation report

1 Publishable Summary

In WP5 DSM focused its attention to weigh process options against each other on the basis of technical and economic feasibility. A boundary condition is the use of catalytic pyrolysis oil (cat-oil) due to its higher phenol concentrations. The first choice was made for an integrated process producing phenol and a bio-fuel suitable for co-feeding to a conventional petroleum refinery. Several synergetic effects can be captured by this approach:

- High utilization of all organic products derived from the pyrolysis process
- Utilization of the stable carbon-oxygen bond in a chemical
- Less severe conditions of a hydrotreatment process necessary for any upgrade of pyrolysis oil to a bio-fuel.
- Contaminated process water can receive a first treatment within the integrated process to remove organic contaminants

To reduce the hydrogen consumption of the process the catoil is first treated in an extraction that removes light organic acids which will save more than 5 kg hydrogen per ton of processed catoil. This is a mayor economic factor.

The integration of the hydrotreatment step will also supply energy to the process needed for downstream separations. The hydrotreatment runs at high temperature (above 250°C) and high pressure (above 50 bar) which in combination with the exothermic reaction will deliver high pressure steam that can be utilized to drive distillation columns, compressors or pumps. The hydrotreated cat-oil will contain aromatic and aliphatic hydrocarbons as well as phenols and phenolic ethers. All other functionalities will be removed. The isolation of phenol and alkylphenol from this mixture is technically not difficult. Either a crystallization or a distillation will be employed to recover this crude mixture which can be further purified using distillation technology.

It is too early to state if this process can deliver phenol at competitive price and quality. Nevertheless no technical show stoppers have been identified so far. There is a large and established phenol market of over 11 million tons per annum which is expected to grow with increasing demand of plastics in all parts of the world.

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3 PFD of the phenol recovery process from catalytic pyrolysis oil

3.1 Introduction

Isolation of a valuable chemical from various primary streams of the conversion of biomass is a challenging task. For isolation of phenol from bio-oils (regardless if from catalytic or fast pyrolysis) especially the properties of the bio-oil determine the process and its economics. Some of the most important properties are shown below.
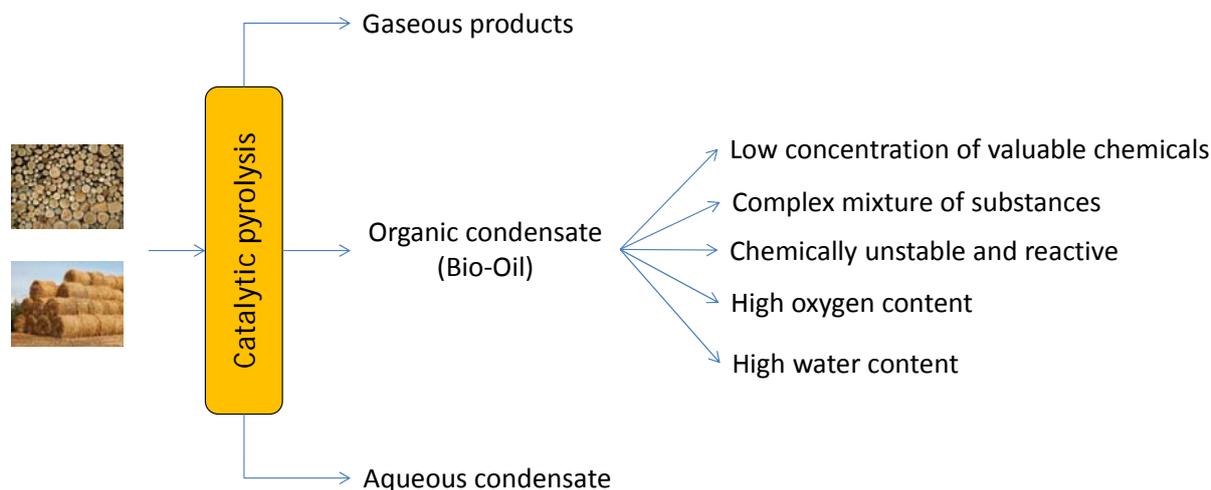(see Figure 1)

Figure 1: Primary conversion of biomass

These challenges are not regularly faces by the chemical or energy industry when producing large scale fuels or bulk chemicals. To ensure that the investment will pay back strategic decisions have to be taken with regard to the products recovered. Several finding from the work carried out in WP3 will be shortly introduced here to elucidate decisions taken that strongly influence the choice of process.

1. A process using all or the largest share of the products originating from the primary conversion process with the least waste production will be in advantage over a process that will co-produce material with little value.
   Therefore a process was chosen where both a chemical (or chemicals) and a transportation fuel will be produced with that covering most liquid products of the pyrolysis unit.
2. The process design has to be optimized for both products at the same time to find the global optimum for the process as a whole rather than to optimize for the maximum possible for one product only. [1]
3. In order for any operation to be economical (a whole process or a single unit operation) the concentrations of the chemical to be recovered has to be above a certain threshold. Generally concentrations of the valuable compound below wt 2% are not acceptable [2].
   For a process to isolate phenol from pyrolysis oil this meant that only a process employing catalytic pyrolysis oil with high concentrations of phenol to begin with will be pursued. [3]
4. The amount of unit operations, additional solvents, acids and bases used have a strong influence on the process as has catalyst stability. A process design with less unit operations is often superior.

In the final report of WP3 several possibilities for process designs are discussed mainly on their technical feasibility. [4] To prove feasibility on lab-scale excluded already several process options since it makes no sense to evaluate process schemes that will not become

operational for physical or chemical reasons. In this report we present the process scheme for which the most critical process steps have been proven on lab-scale. We will also discuss the choices to be made when more process information is available.

3.2 Process Flow Diagram

We consider for this study the pyrolysis process to be out of scope of our discussion. Another important assumption is that we expect several pyrolysis units to deliver products to a central conversion plant whose products are phenol and a bio-fuel for further upgrading in a fuel refinery. The now envisaged process is shown in Figure 2.
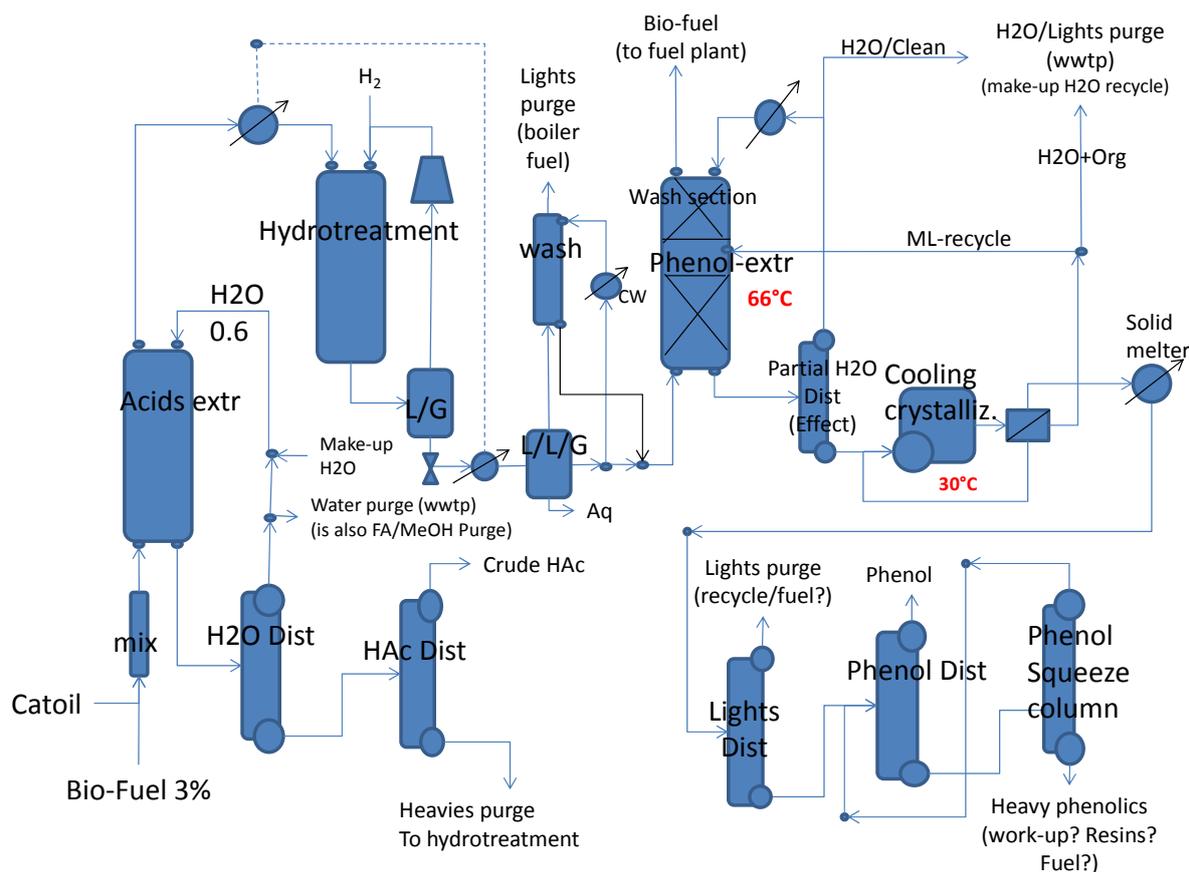

Figure 2: Process flow diagram of phenol and bio-fuel process from Cat-oil

On process level choices where the different process steps will be located can be made. The acid extraction with its H_2O and AcOH distillation for example can be located next either to the pyrolysis plant or at the central conversion unit. Location next to the pyrolysis plant has the benefit of integrating surplus heat available in this the pyrolysis plant with those distillation steps. In principle these unit operations are capable of treating the aqueous condensate from the pyrolysis as well. This enables the recovery of any valuable compounds in the aqueous condensate and decrease the organic load for the waste water treatment plant (wwtp). At this stage of research it cannot yet be determined whether this option is more beneficial then concentration these fractions on the central conversion location where capital investments will be lower.

Another choice depending on the quantity of heavy organic side streams is to either utilize them for hydrogen production to support the hydrotreatment unit or via another pathway.

In the following sections each functional unit and its purpose in the plant will be further explained.

3.3 Acid extraction and recovery section

One of the main cost drivers for the variable costs of this process will be the cost of the hydrogen needed in the hydrotreatment section. Hydrogen production is expensive and the use of must be limited. If the cat-oil is directly hydrotreated hydrogen will be used to remove oxygen from short and long chain oxygen containing molecules. It is necessary to remove oxygen from the long chain molecules to be used as fuel components.

Table 1: acetic acid concentrations and hydrogen uptake

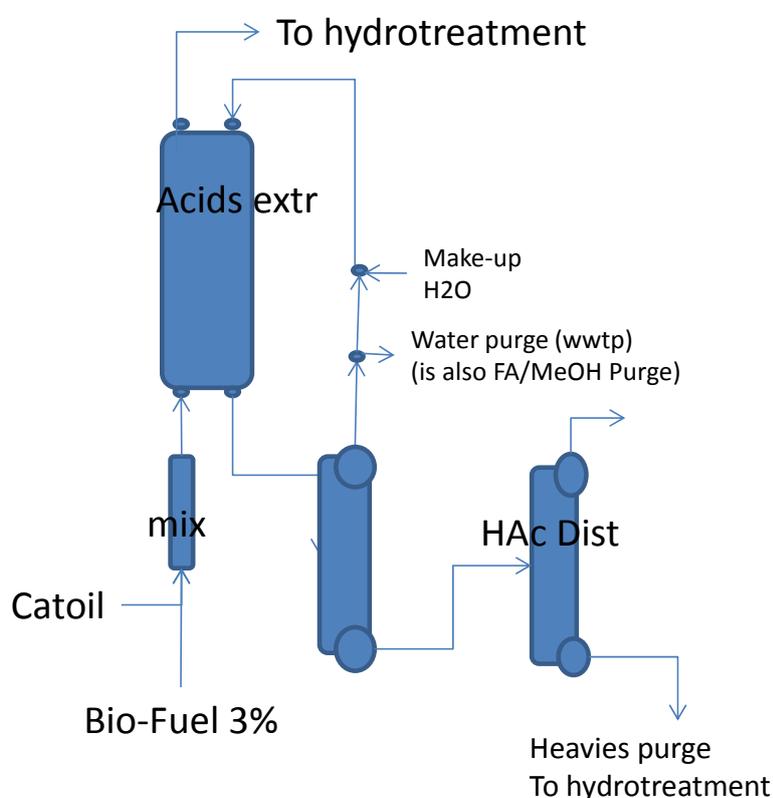|	AcOH in wt%	AcOH in kmol/t	H_2 in kmol/t	H_2 in kg/t
CP bio oil 026-035	4	0.67	2.00	4.00
BIOB 2069-029	8.5	1.42	4.25	8.49
BIOB 2057-018	5.5	0.92	2.75	5.50

Figure 3: Acid extraction and recovery section

The hydrotreated short chain molecules though will be useless as transportation fuel since they are gaseous. In addition these short chain molecules such as acetic acid, propionic acid or methanol are present in high concentrations (acetic acid ~5wt%) and consume comparably a large amount of hygrogen. For example for every equivalent of acetic acid 3 equivalents of hydrogen are consumed. With the analytical data provided in D3.1 a saving in hydrogen consumption for acetic acid is given in Table 1. [3] It can be concluded that the removal of acetic acid results in a average saving of 5kg hydrogen per t treated catoil.

Fehler! Verweisquelle konnte nicht gefunden werden. shows the acid extraction section of Figure 2. The first treatment of this section is to mix the catoil coming from the pyrolysis reactor with a light organic fraction (3wt% addition in relation to the catoil). This has proven to be necessary to keep the cat-oil at low viscosity after the acid extraction. The light organic

fraction may well be part of the bio-fuel produced in the phenol extraction section thus creating a small recycle and not introducing a new substance to the process.

The second operation is an extraction of the treated catoil with water to extract small organic acids and alcohols. This unit operation has the purpose to reduce the acetic acid concentration to below 0.1wt%. On the other hand this will cause the loss of valuable product to the water phase. To recover this product and to recycle the water two further unit operations are necessary. The diagram shows two distillation columns where the first one is responsible to remove water. The water recovered will be recycled to the acid extraction. MeOH and formic acid which will accumulate to some extent in the water and a purge in combinationwith addition of make-up water may be necessary. The second column will produce crude acetic acid but its main function is to recover the lost valuable products that are present in this process stream. Depending on the composition of this heavies purge it can either be added to the hydrotreatment or directly to the phenol extraction.

Next to two distillations also a combination of extraction and distillation is possible. A decision is with the given data not yet possible it will amongst others depend on the location of this section. If the aqueous condensate from the pyrolysis unit will have to be treated an extraction/distillation can also be economical.

3.4   Hydrotreatment section

The purpose of the hydrotreatment section is to reduce the oxygen content of the catoil. For this process the conditions of the hydrotreatment have to be chosen such that the phenol oxygen bond is not broken. Since it is the strongest oxygen-carbon bond in the reaction mixture this can be achieved by lowering the pressure and temperature of this operation in comparison to regular hydrotreatment operations.

Here only a brief explanation will be given, a more extensive discussion is part of D5.4 and the final report of Workpackage 5.

The acid lean catoil from the acid extraction section is first heated-up via a heat exchanger and subsequently pumped under high pressure into the hydrotreatment reactor. For efficient pre-heating of the feed and cooling of the hydrotreatment product to feed heat-exchange is applied. High pressure hydrogen is applied to the reactor as well. After the reaction the products are fed to a first gas/liquid separator at high pressure to be able to recycle unreacted hydrogen against low recompression cost.. [?? Not important at this point because the vapor part of light hydrocarbons can just be circulated with H2 most lights will leave dissolved in liquid phase under pressure].

The liquid is further depressurized and cooled down. Process heat recovered here offers the possibility of energy integration to lower the variable costs of the process. Since the reactions in the hydrotreatment reactor are strongly exothermic also inter-bed coolers will be applied to produce high pressure steam. This will supply likely a large portion of the process heat needed in the other sections. After depressurizing the product stream is fed to a liquid/liquid/gas separator. The main function of this unit operation is to remove light hydrocarbons that are not suitable for transportation fuel application as vapor product. To ensure that entrained higher hydrocarbons do not leave the process a wash column with the cooled liquid product from the L/L/G separator is installed. These streams will be combined again and be send to the phenol extraction section.
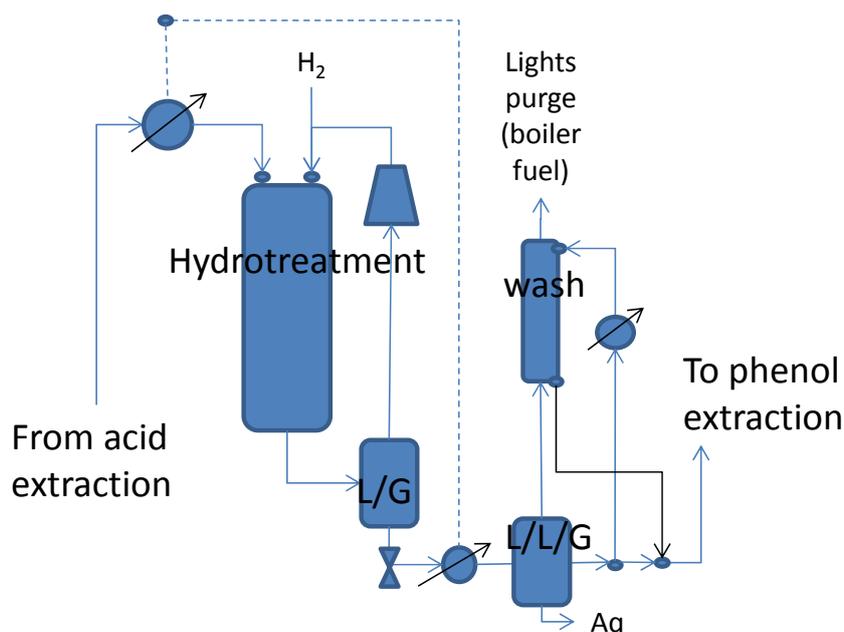
Figure 4: hydrotreatment section

If separation of the water formed during the hydrotreatment is necessary at this step is still undecided. Depending on the temperature of the water it will contain several wt% of valuable phenols which can be recovered in the phenol extraction section if the streams are treated in a combined fashion.

3.5 Phenol extraction section

The main purpose of the phenol extraction section is to remove phenol and alkyl-phenols from the hydrotreated bio-oil. This section will also be most relevant for the water balance of the whole process since here clean (phenol/organic acid/ hydrocarbon free) water will be recovered.
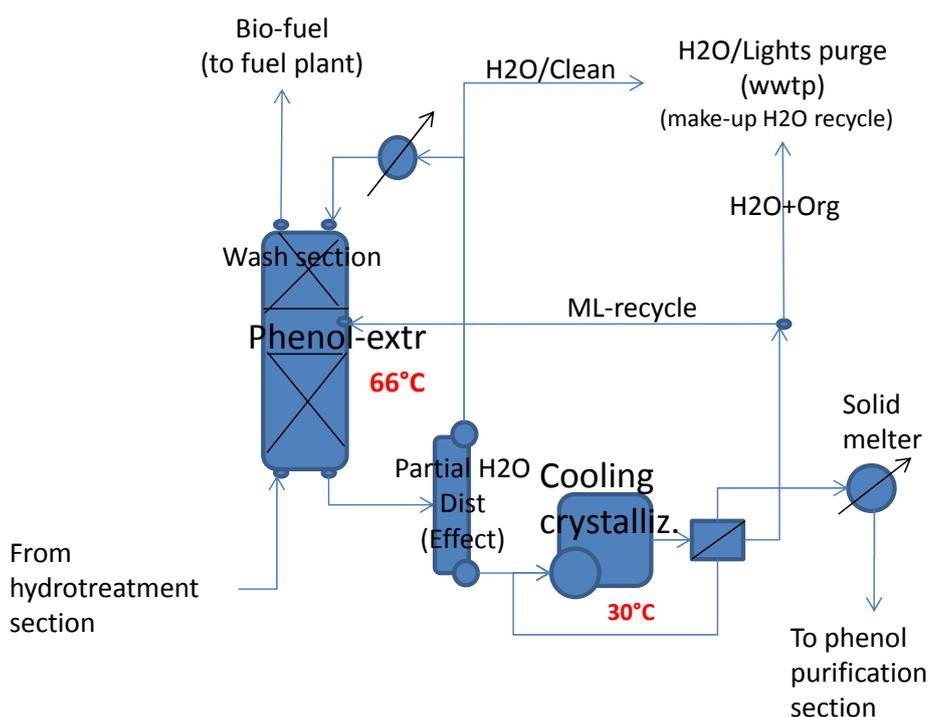

Figure 5: phenol extraction section

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The hydrotreated catoil will be contacted with a phenol lean mother liquor (ML) in an extraction column. The temperature of this unit operation will be above 66°C where phenol is fully miscible with water. This will give a phenol and alkylphenols rich aqueous stream and a phenol lean cat-oil stream. The remaining phenol and alkylphenols will be separated in the wash section of the column where clean water will be used to recover the phenol. This unit operation will deliver phenol lean bio-fuel which is send for further upgrading to a refinery.

From the phenol and alkylphenols enriched aqueous phase first water will be distilled off. The quality of the water has to be such that it can be used as wash water in the phenol extraction column. The excess water will be send to a wwtp or other process steps needing water. The remaining aqueous phase will contain phenol and alkylphenols in high concentration which will spontaneously phase separate or crystallize at temperatures below 30°C. The crystals will be filtered, melted and send to the phenol purification section (alternatively via cooled wall crystallization). The mother liquor will be recycled to the phenol extraction and part of it purged to the wwtp. Attention has to be given at this stage to since wwtp do not allow phenols to be present above few ppm in this stream.

As an alternative for crystallization, concentration of phenol may also be done in a more energy demanding water removal step consisting of effect evaporation in multiple columns followed by a distillation to remove the last amount of water before the phenol containing bottom stream is fed to the phenol purification section.. Though not shown in the figures below it is an option if the crystallization proves to be difficult due to impurities present.

3.6 Phenol purification section

The function of this section is to produce purified phenol at high yield. To achieve this in a mixture of close boiling alkylphenols three distillation columns are necessary. The first one will remove lights such that the losses of phenol are minimal. The second column will produce phenol at a high purity expectedly with 80-95% yield per pass. The phenol squeeze column will produce a phenol lean heavy alkyl phenol fraction at the bottom of the column. Here as in the lights column the phenol losses will be minimal. The top fraction containing alkylphenols and phenol will be recirculated to the phenol column to allow another pass of the material thus increasing the phenol yield of the section as a whole.
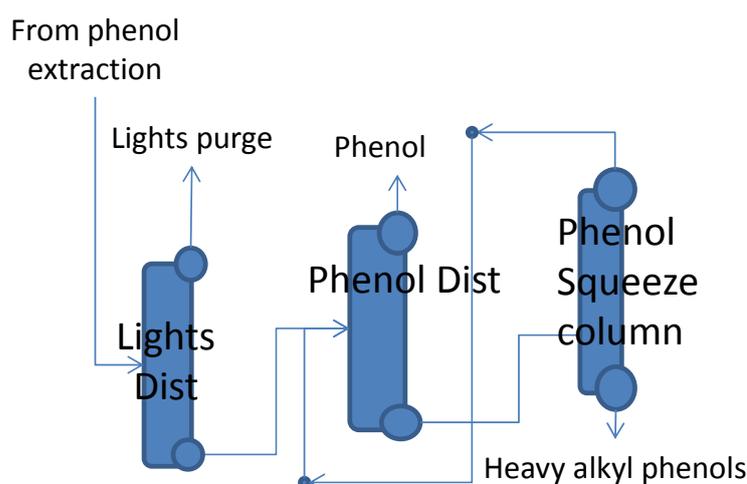

Figure 6: phenol purification section

4 Economic perspective

Phenol has a worldwide production capacity of 11.000 kta (kilotons per annum). The uses of phenol in chemical industry are manifold. 37% of all phenol produced is manufactured further to Bisphenol-A which is used in high grade polycarbonates and epoxy-resins. A second large market for phenol is phenol-formaldehyde resins which capture 31% of the world's production. The third biggest demand for phenol is the production of caprolactam with 8% (728 kta in 2010) of the total phenol production [5].

A detailed discussion of the economic perspective of phenol was given in D3.1 and will not be recapitulated here. Only the main aspects will be repeated. For more details please see [3].

All basic requirements described in D 3.1 are covered by the process proposed:

1. utilization of the starting material with the highest phenol concentration
2. continuous process operation
3. no stoichiometric input of inorganic salts, acid or bases
4. no stoichiometric inorganic waste produced.
5. generally low E-factor [6] due to co-utilization of chemicals and fuels
6. solvents for extraction are non-chlorinated and inexpensive (water)

If the process itself is capable of producing phenol at sufficient quality and with competitive prices cannot be determined at this stage. Further investigations and pilot trials of yield and purity determining unit operations will have to be performed to answer this question.

5 Bibliography

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[5] M. W. M. K.-B. M. Weber, "Phenol," in *Ullmans Encyclopedia of Industrial Chemistry*, Weinheim, Wiley-CVH Verlag GmbH, 2012, pp. 503-519.