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## Production of Discrete Oxygenated Target Chemicals from Pyrolysis Oil

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### Purpose of the work

Biomass is a promising renewable feedstock for chemicals. Pyrolysis of biomass produces a dark, brown colored liquid (bio oil), which consists of a complex mixture of oxygenated hydrocarbons, water and char. The key advantage of the produced bio-liquids over crude oil is their high content of oxygenates.

The main objective of this project is the development of selective affinity extraction technology for the isolation of discrete target oxygenated chemicals (alcohols, aldehydes, ketones, phenolics and sugars) from the various bio-liquids produced. The focus of this work is on main aldehydes/ketones in pyrolysis oil: furfural, glycolaldehyde and acetol.

### Approach

Reactive extraction seems a promising method to isolate carbonyl compounds since conventional techniques are unfeasible. There are three possible sources for the desired chemicals: the pyrolysis oil itself and, after water addition, the polar aqueous phase and the apolar oil phase. A NaHSO<sub>3</sub> solution can be used to extract aldehydes and ketones directly from the pyrolysis oil.

### Scientific innovation and relevance

At this moment, no commercial isolation processes are known for specific single components (molecules) in the bio-oil. A promising isolation process for groups of chemicals is reactive extraction, which is highly selective towards the chemicals of interest.

### Results

Addition of water to pyrolysis oil will cause a phase separation between aqueous and organic phases. Aldehydes and ketones are polar compounds; hence, they will be dissolved to the aqueous phase during phase separation. However, some of the target chemicals have a limited solubility in water (e.g. 8.1 g furfural in 100 g water at 20 °C). For these chemicals, water capacity as extracting solvent is limited; hence, a bisulfite solution is used to increase the capacity of water as the extracting solvent. In order to isolate the extracted chemicals, back-extraction was carried out with toluene, octanol or hexanol as suitable solvents. In Table 1, the results of the forward and the back-extraction are shown.

Table 1. Efficiency of forward and back extraction

Compounds	Reactive Extraction	Toluene		Octanol		Hexanol	
		Back extr	Total	Back Extr	Total	Back Extr	Total
Furfural	85%	65%	55%	40%	35%	57%	48%
Acetol	99%	5%	5%	10%	10%	15%	15%
Glycolaldehyde	~100%	<<	-	<<	-	<<	-

### Conclusions

Separation of selected aldehydes from pyrolysis oil is possible by reactive extraction with an aqueous NaHSO<sub>3</sub> solution with high efficiencies. The most common suitable solvent for the recovery of furfural and acetol is octanol, because it has a sufficiently different boiling point from both aldehydes.

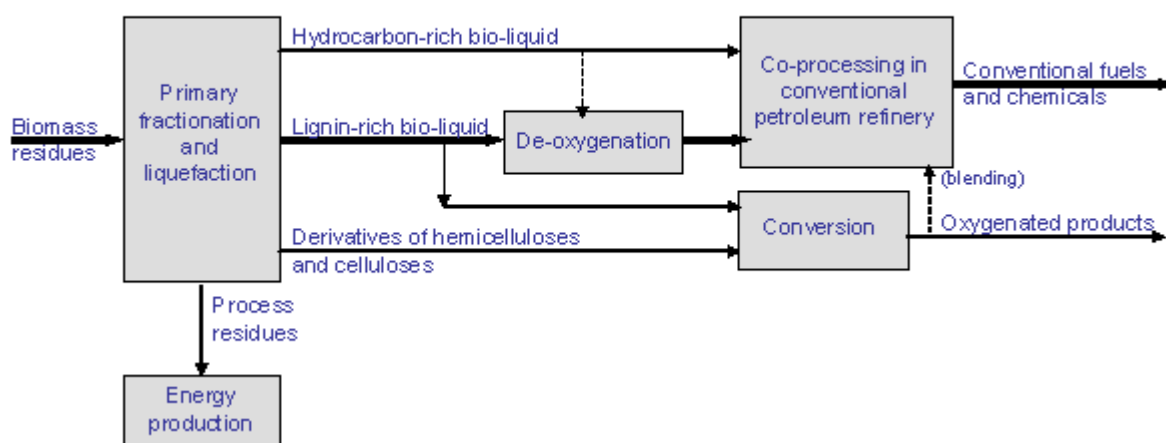
## Production of Discrete Oxygenated Target Chemicals from Pyrolysis Oil

Supplement to the abstract

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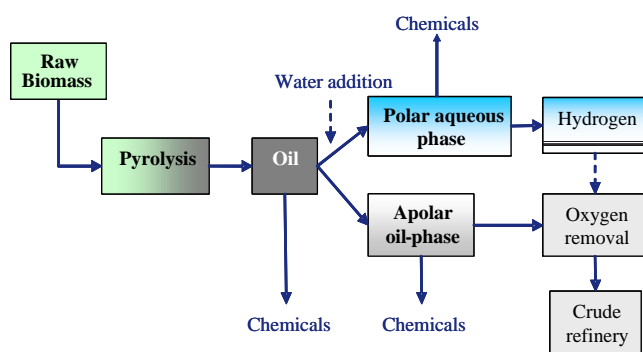
### Introduction

The main aim of this project is to upgrade biomass-derived liquids so that they are suitable for co-processing in conventional refinery units. Hence, no new installation will be required for fuel production and so the total costs can be minimized. In addition, the extraction of high-valuable chemicals from the bio-liquids prior to the co-processing will be developed to achieve a biorefinery concept, as shown in Figure 1. This work is carried out within the European Project BIOCOUP.



**Figure 1** Overall biorefinery concept

Biomass residues (e.g. forest residue, industrial waste from pulp and paper industry, organic municipal waste, etc) are liquefied by means of flash pyrolysis to produce pyrolysis oil. The hydrocarbon fraction of the pyrolysis oil can then directly be co-processed in the petroleum refineries. The pyrolysis oil has a high oxygen content; hence, a de-oxygenation step is necessary prior to co-processing. Besides, the derivatives of hemicelluloses and celluloses are



**Figure 2.** Schematic view of the process from biomass to pyrolysis oil and the possibilities for chemical extraction

valuable chemicals, e.g. hydroxyaldehydes and sugars, thus this fraction can be extracted to produce oxygenated bio-chemicals.

In Figure 2, an overview of the process and the possibilities for chemical extraction are shown. There are three possible sources for the desired chemicals: the pyrolysis oil itself and, after water addition, the polar aqueous phase and the apolar oil phase. A  $\text{NaHSO}_3$  solution can be used to extract aldehydes and ketones directly from the pyrolysis oil.

One of the important reactions with aldehydes and ketones that are of interest in this project is the addition of bisulfite ion as presented in Figure 2. This reaction has been long used as identification and purification of carbonyl compounds. Bisulfite reacts selectively to carbonyl compounds, thus the forward reaction can be used as a purification step. The aldehyde-bisulfite salt is then crystallized and separated from the mixture. For the recovery, the equilibrium is shifted to the left and the pure compound can be obtained. Some very reactive aldehydes, such as formaldehyde, are often available in their stable bisulfite adduct form. In this project, this reaction is used to separate the carbonyl compound from other components of pyrolysis oil.

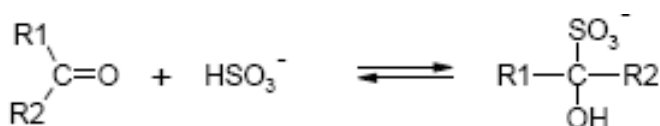


Figure 2. Bisulfite adduct formation of aldehydes and ketones

### Conceptual Process Design

The main objective of this project is to provide a conceptual design for the separation of aldehydes and ketones from pyrolysis oil. Distillation is not a suitable option for pyrolysis oil fractionation. The liquid is chemically unstable and the components are prone to react with each other into high molecular weight compounds and water. Heating the liquid will increase the reactivity of the compounds. Besides, due to the low content of aldehydes and ketones in the feed, distillation is economically not feasible. Solvent extraction appears to be one of the promising ways to separate the target chemicals from the pyrolysis oil.

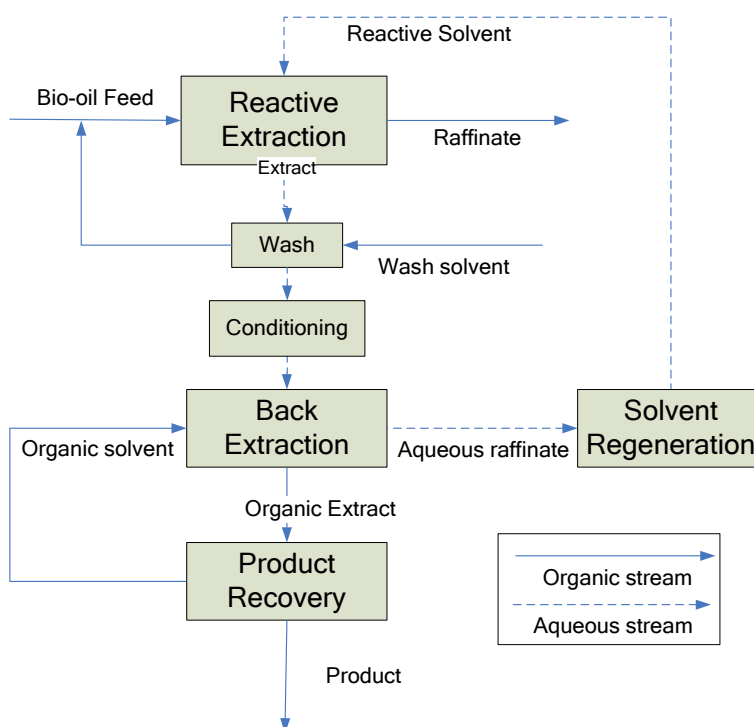


Figure 4. Conceptual scheme of aldehydes/ketones extraction from pyrolysis oil

The conceptual scheme of the process is presented in Figure 4. The first step is a reactive extraction, where an aqueous bisulfite solution is used to extract the target chemicals. Bisulfite will react highly selective with aldehydes and ketones, thereby increasing the overall distribution coefficient of those compounds. However, the water that is originally present in

the pyrolysis oil will also transfer to the aqueous phase, so the bisulfite concentration will decrease. All the water-soluble compounds from the pyrolysis oil will dissolve in the aqueous phase as well, for instance low-boiling acids and anhydrosugars. The objective in this step is to achieve highest yields of target chemicals. The factors that influence the reactive extraction are bisulfite concentration and volume ratio.

The extract is then washed by an organic solvent, to remove all the non-polar organic materials that are dissolved in the water phase during extraction. The aldehydes and ketones are dissolved in the extract in the form of bisulfite salts; hence, they will not be removed by the organic solvent.

The next step is to recover the aldehydes and ketones from the aqueous extract by means of a back extraction by an organic solvent. Solvent selection is crucial in this step, in order to get a high recovery of target compounds.

After all the target chemicals are extracted in the organic phase, the organic solvent has to be removed and recycled, so an aldehyde/ketone fraction is obtained. This fraction has to be further fractionated to get single compound fractions.

The last step is the regeneration of the bisulfite solution. The bisulfite concentration has to be increased to the original concentration, and the water-soluble compounds have to be removed.

## Results

The experimental results show that the target chemicals can be extracted from the pyrolysis oil with a high efficiency, 85 to 100%. Toluene is the best solvent to recover furfural, with a yield of 65%, whereas hexanol is the best solvent for acetol, with a yield of 15%. However, for the sake of solvent separation, hexanol is not selected as the solvent, because it has a similar boiling point as acetol and furfural. For that reason, octanol was selected instead, because it has a sufficiently different boiling point from both aldehydes. The yield of the forward and backward extraction of the compounds is listed in Table 11.

**Table 1. Experimental results of reactive extraction and back-extraction.**

Compounds	Reactive Extraction	Toluene		Octanol		Hexanol	
		Back extr	Total	Back Extr	Total	Back Extr	Total
Furfural	85%	65%	55%	40%	35%	57%	48%
Acetol	99%	5%	5%	10%	10%	15%	15%
Glycolaldehyde	~100%	<<	-	<<	-	<<	-

However, glycolaldehyde, the most abundant compound in the pyrolysis oil, cannot be recovered by back-extraction. In aqueous solution, glycolaldehyde is present as an equilibrium mixture of following structures:

- dioxane dimer (9%)
- monomer (4%)
- hydrate (70%)
- dioxolane dimer (17%)

In solution, it reacts with the solvent to form a stable solution. Particularly in an aqueous solution, most of the glycolaldehyde molecules form a hydrate, which implies a strong bond with water. Therefore, another method has to be found for the recovery of glycolaldehyde.

## Conclusions

Separation of selected aldehydes from pyrolysis oil is possible with reactive extraction with a NaHSO<sub>3</sub> solution with high efficiencies. The most suitable common solvent for the recovery

of furfural and acetol is octanol, because it has a sufficiently different boiling point from both aldehydes.