Evaluation of Transition Metal Catalysts for Biphasic Oxidative Depolymerization of Kraft Lignin

by

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Abstract

To decrease the dependency of fossil-based raw materials in society, and with that, the chemical industry, new and sustainable raw materials need to be investigated. Lignin is an abundant aromatic biopolymer, that can be used to produce, e.g. aromatic fine chemicals through depolymerization. In this master's thesis, different homogeneous and heterogeneous catalysts were screened for oxidative depolymerization of Kraft lignin in a biphasic system. Iron, copper- and cobalt-salts with different counter ions were screened homogeneously, and iron-copper, iron-cobalt, copper-cobalt and monometallic iron catalysts on zirconia support were screened heterogeneously. Samples were analysed and products quantified using ultra-high performance liquid chromatography coupled with high resolution mass spectrometry. The most abundant identified aromatic product for most catalysts was vanillin, reaching yields of up to 1.1 wt% with iron(III)chloride as homogeneous catalyst, which is an increase of 175% compared to using no catalyst. The difference between the best performing catalysts was not significant, so it is difficult to determine the most suitable catalyst for the system. In general, iron-based catalysts seem to favour a higher selectivity for vanillin, while copper catalysts produce a more diverse product pool. Among the homogeneous catalysts, the chloride salts generally gave higher vanillin yields. When nitrate salts were screened as catalysts, 5-nitrovanillin and other nitrated aromatics were formed, indicating that the catalysts were functioning as reagents.

Populärvetenskaplig sammanfattning

Lignin är ett ämne som finns i alla växter och bidrar med stabilitet genom och skydd mot angrepp från bland annat svampar och bakterier. Ämnet produceras i huvudsak som en biprodukt när träd används för att producera pappersmassa genom olika metoder, och omkring 100 miljoner ton lignin produceras varje år. Tack vare att lignin har en speciell struktur, där aromatiska molekyler är sammanlänkade i en kedja, kan lignin användas för att tillverka värdefulla kemikalier, i synnerhet vanillin. I dagsläget produceras majoriteten av dessa kemikalier från fossilbaserade råvaror och de kan användas som smak- och doftämnen i livsmedel och kosmetika, för tillverkning av plast och i läkemedelsproduktion. Genom att hitta en effektiv metod för att bryta ner lignin till aromatiska kemikalier kan fossila råvaror därmed ersättas av en billig och hållbar råvara som i dagsläget mestadels förbränns för att utvinna energi.

Det finns olika metoder för att omvandla lignin till värdefulla kemikalier, men alla utgår ifrån principen att klippa länkarna mellan de aromatiska enheterna i ligninet. I det här projektet har ett speciellt system använts, där ligninet bryts ner i saltsyra vid höga temperaturer, samtidigt som de värdefulla produkterna extraheras till en annan fas, bestående av oktanol, som skyddar dem från att ytterligare brytas ned. Syrgas används som ett oxideringsmedel som bidrar till att bryta bindningarna i ligninet. Eftersom lignin är ett komplext ämne som skiljer sig mycket beroende på hur det har utvunnits och vilken växtart det kommer ifrån, så kan det vara svårt att uppnå en hög produktion av dessa aromatiska kemikalier. Katalysatorer kan användas, för att snabba på och underlätta nedbrytningen. Katalysatorerna kan antingen vara salter som är upplösta i reaktionsvätskan - homogena katalysatorer - eller i en fast form som gör det lätt att separera dem från reaktionsvätskan och återanvända dem – heterogena katalysatorer. I det här projektet har olika järn, koppar och koboltsalter testats som homogena katalysatorer, och heterogena katalysatorer med samma metaller i olika kombinationer.

När katalysatorerna testades homogent visade det sig att järn har en positiv effekt på bildandet av vanillin, medan det bildades fler olika sorters produkter när koppar användes. Kobolt producerade minst vanillin. Det visade sig även att det bildade en helt egen typ av molekyler när nitratsalter användes i reaktionen, nitrerade aromatiska kemikalier, i stället för vanillin och andra kemikalier som bildades av de andra katalysatorerna. När de heterogena katalysatorerna testades fanns samma trender att järn främjar vanillinproduktion och koppar främjar bildande av flera olika sorters ämnen. Trots att detta system med två faser tidigare har uppnått en effektiv omvandling av lignin till vanillin på 7 viktsprocent så uppnådde detta system maximalt 1.1 viktsprocent, vilket kan ha berott på skillnader mellan ligninet som användes och att syrgasen tog slut i systemet.

Contents

1 Introduction

To decrease modern society's dependency on petroleum-based raw materials, new and sustainable raw materials and processes need to be explored to find ways to produce fuels and organic chemicals. Lignin, an abundant biopolymer present in all plants, could be a sustainable alternative as a raw material for the production of fine chemicals due to its aromatic structure. It is mostly produced as a by-product from the pulp and paper industry, making it a sustainable and cost-effective raw material.[1-3]Although the production of aromatics from lignin has been shown to have a smaller environmental impact than using crude oil[4, 5], there are several challenges that need to be addressed for lignin to be able to replace fossil-based raw materials. The main challenges in the field are low yields of aromatic monomers, and the heterogeneous nature of lignin due to differences between plant species and extraction methods[3, 6].

Biphasic depolymerization of lignin (BPD) is a novel method, through which high yields of aromatic chemicals have been achieved[7]. The method combines catalytic oxidative depolymerization of lignin in an acidic aqueous phase with protective extraction of the aromatic monomers in an octanol phase. The system has been shown to increase yields when compared to the corresponding monophasic system. It also allows for easy catalyst recovery, even for homogeneous catalysts, as they are insoluble in the organic phase[8].

1.1 Project description

In this work, different transition metal catalysts were screened for depolymerization of Kraft lignin (Indulin AT) in the BPD system. Cu-, Fe- and Co-based catalysts were tested homogeneously and heterogeneously. For the homogeneous testing, different counter ions were also screened to evaluate their impact on the lignin depolymerization. The reaction products are characterised using ultra-high performance liquid chromatography coupled with high-resolution mass spectrometry (UHPLC-HRMS) and monomeric yields calculated.

1.2 Aim

The aim of this work is to find a suitable homogeneous and/or heterogeneous catalyst for biphasic oxidative depolymerization of Kraft lignin, to maximise the yields of high-value aromatic monomers. An additional objective is to investigate the depolymerization product pool for the different catalysts.

1.3 Scope

Homogeneous and heterogeneous catalysts were screened for lignin depolymerization in a biphasic system. The products will be identified and quantified using UHPLC-HRMS and the performance of the catalysts will be evaluated based on the production of aromatic monomers. Basic characterization of fresh catalysts (X-ray diffraction (XRD) and nitrogen physisorption) was also performed. Characterization of spent catalysts and optimization of process conditions and heterogeneous catalysts was beyond the scope of the thesis.

1.4 Disposition

In this thesis, a brief introduction to lignin and how it is produced is given, followed by how it can be used as a raw material for production of high-value chemicals and what is needed for industrial production. An overview of the BPD is also given. The introduction is followed by a materials and methods section where the experimental methods are described for the catalyst screening in the BPD system. How the heterogeneous catalysts were produced is also explained as well as how they were characterised, and an overview of the chemical analysis and data analysis were performed is also given. The results are then presented and discussed, and summarised in a final conclusion section.

Background

In this section, a brief overview of the properties of lignin and its role in plants is given. Different methods of producing chemicals using lignin as a raw material and how they can be applied industrially are also described.

1.5 Lignin

Lignin is the second most abundant biopolymer on earth and has a unique aromatic structure.[3] The amorphous polymer is present in all plants and acts as a glue to give structural integrity[1] and biological and chemical resistance[9]. Around 100 million tonnes of lignin is produced globally per year as a by-product in the pulp and paper industry[10], where it is usually burned to recover energy.[3] Lignin can be used in macromolecular applications and to produce biofuels[1, 3], but the most unique feature of the biopolymer is its aromatic structure which makes it a suitable raw material to produce high-value aromatic chemicals[1, 11-13].

The lignin structure and composition vary depending on plant species and the extraction method used to separate the lignin from the rest of the biomass. It can also vary between individual plants of the same species, due to external factors and stress. The lignin is synthesised within the cell walls of plants[14] through polymerization of three different phenolic monomers: *p*-coumaryl, coniferyl and sinapyl alcohol[1, 15]. This results in a polymer consisting of three different aromatic residues *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S), depicted in Figure 1. The ratios between these three monomers vary depending on lignin species, with softwood lignin consisting almost exclusively of G-units with a small[14] fraction of H-units. Hardwood lignin has more equal proportions of S- and G-units with some H-units, and grass lignins have a more equal distribution of all three[3].

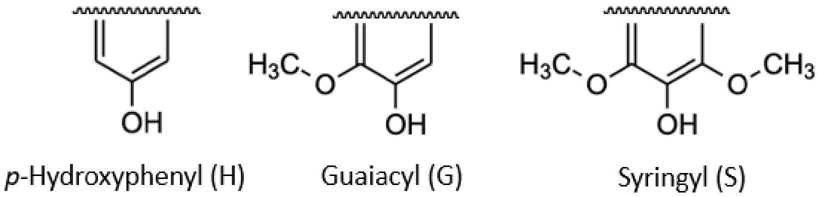

Figure 1: Three types of aromatic residues in lignin.

In simplified terms, there are two types of linkages between the aromatic monomers within lignin: carbon-carbon (C-C) and ether (C-O) bonds. The C-C bonds are much more robust than the ether bonds, which are easier to break[3]. The monomers can be bound together at the 1, 5, and β-position. This results in the C-O bonds α-O-4, β-O-4 and 4-O5 and the C-C bonds β-β, β-5, β-1, and 5-5 bonds, where the β-O-4 is the most common linkage in the lignin structure within plants. The formation of C-C bonds is hindered by substituted groups on the aromatic ring, lignin with more S-units will therefore have more ether linkages due to steric hindrance from the methoxy-group in the 5-position. Depending on the process of isolation the lignin from the rest of the biomass, the ether linkages can be condensed to form C-C bonds instead. To produce aromatic chemicals from lignin, the lignin needs to be depolymerised, meaning that these bonds must be broken.[3, 12, 14]

1.5.1 Types of lignin

As previously mentioned, lignin is mostly produced as a by-product from the pulp and paper industry. These so-called technical lignins can be produced through several different pulping processes, such as Kraft pulping, sulphate pulping, soda pulping and more. The main objective of all the processes mentioned is to obtain a pure carbohydrate fraction to produce paper products. How the process affects the lignin removed is not taken into consideration, as it is only used for energy recovery[14, 16]. This means that the operating conditions employed in pulp mills are very harsh, operating at high pH and temperature which causes condensation of ether bonds and introduces impurities into the lignin structure[3, 16-18]. This in turn makes the lignin difficult to valorise into high-value aromatic monomers, since there is a higher amount of the robust C-C bonds. In spite of this, technical lignins could play an important part in the transition away from fossil-based raw materials in the chemical industry due to the high production volumes worldwide[3].

Kraft lignin, which is the type of lignin used in this project, is produced as a waste stream from the Kraft pulping process and represents 95% of the chemical pulp produced worldwide[13]. In this process, wood chips are treated at high temperature and pressure in an alkaline mixture of sodium hydroxide and sodium sulphite. The remaining solids, mostly consisting of cellulose, are further treated to finally produce paper and cardboard products. The liquid, called black liquor is usually used as inexpensive fuel to power the process itself, but the lignin can be recovered through precipitation by lowering the pH of the black liquor, followed by filtration, and drying[2, 14, 16]. Typically, more lignin is produced in the process compared to the amount that is required to meet the energy demand in of the process[13]. This gives plenty of Kraft lignin to be used for production of high-value chemicals, but it is a highly condensed lignin with very few ether bonds, making up less than 10% of the total linkages within the lignin structure[19].

To preserve the lignin structure as close to its native form inside of the plant, new methods have been developed to isolate lignin from biomass. One of these so-called *lignin first*-methods is aldehyde-assisted fractionation (AAF) wherein the biomass is separated into three fractions: lignin, cellulose, and hemicellulose. Formaldehyde or acetaldehyde is used as a solvent, which protects the ether bonds in the lignin from condensation, resulting in a more native-like lignin[18]. The advantage of these methods is that it results in a lignin with a higher percentage of ether-bonds, which makes it better suited as a raw material for production of aromatic chemicals compared to technical lignin, as much higher yields are achievable. This innovation presents new possibilities for future biorefineries where all three main fractions of the biomass can be utilised to produce valuable chemicals[17]. Although this technology allows for higher yields of aromatic monomers, it is still a very new concept that is not as well established as the traditional pulping processes.

1.6 Fine chemicals from lignin

In this section, different methods for producing chemicals from lignin are discussed and compared. In the last section, biological conversion of lignin-derived chemicals for production of sustainable plastics is described.

1.6.1 Products from lignin

Lignin has a wide range of uses, both as raw material for production of aromatic chemicals and in macromolecular applications. Lignin can be used as a dispersing or binding agent, or to produce activated carbon, carbon fibres, and more.[3] The aromatic chemicals that can be produced from lignin include vanillin, guaiacol, phenol, and syringealdehyde[3, 20]. The aromatic monomers that can be produced from lignin vary between plant species, extraction method and method of depolymerization. Reductive depolymerization tends to yield less functionalised aromatic monomers, such as benzene, toluene and xylene, or propylphenol, which can be used as platform chemicals and fuels[1, 21, 22]. Oxidative depolymerization could however generate functionalised high-value aromatics that can be used to produce fine chemicals[1, 3]. The products from lignin depolymerization have several different applications, such as food flavourings and as precursors to plastics, pharmaceuticals, herbicides, among others. The majority of these chemicals are currently being produced from fossil-based raw materials. A small amount of lignin-based vanillin (around 15% of the total vanillin production) is presently being produced by the Norwegian company Borregaard, which has used lignosulfonates as feedstock for over 50 years[3, 6].

1.6.2 Methods for depolymerization

A promising method for lignin depolymerization industrial production of aromatic monomers from lignin is oxidative depolymerization. In nature, oxidative degradation is also the primary method used by fungi and bacteria to break down lignocellulosic biomass. Oxidative depolymerization works through breaking the linkages between the aromatic units in the lignin oxidatively. The advantages are that it requires relatively mild operating conditions and can produce high-value and highly functionalised aromatic monomers which can be used for pharmaceuticals, plastics, food flavouring, etc[1, 3, 12]. Reductive depolymerization, on the other hand, produces simpler phenolic compounds such as benzene, toluene, and xylene, and propylphenols[1, 22].

There are several challenges when it comes to lignin depolymerization. The condensed nature of technical lignins makes it difficult to achieve high yields of aromatic monomers and fully convert the feed into valuable product. The variations in the lignin structure could also pose challenges in keeping the process performance consistent. This also means that using model compounds often gives misleading results that are different to when real lignin is used as feedstock[3, 19]. The challenge with oxidative depolymerization is the risk of over-oxidation of the products, which can result in ring-opening of the aromatics[3, 23]. There is also the issue of monomer repolymerization, resulting in dimers, trimers, and oligomers. This occurs due to the formation of radical species by the oxidation, making side reactions difficult to control[24].

Catalysis can play an important part in utilizing the full potential of lignin depolymerization and to make the process more attractive for industrial applications in biorefineries and pulp mills[25]. Both homogeneous and heterogeneous catalysts have been studied for the purpose of oxidative depolymerization, and they have their own advantages and disadvantages. Homogeneous catalysts can penetrate the three-dimensional lignin structure and can easier reach the targeted linkages, while heterogeneous catalysts can easily be separated from the products and be reused. The downside to using heterogeneous catalysts is that they run the risk of being deactivated by bio-char formation on the surface[12] and catalyst poisons[26]. They might also be limited by steric hindrance in the lignin structure[12]. Cu-, Fe-, Co-, Mn-, Mo- and V-based catalysts have shown promising results when used as catalysts in oxidative lignin depolymerization[1, 3].

The oxidant used in the depolymerization can have a significant impact on yields and selectivity of the reaction. Hydrogen peroxide is a common oxidant which is both effective and inexpensive. The downside to using this is that it is very highly oxidizing, which can result in over oxidation of the aromatic monomers into aliphatic compounds. Oxygen gas is another cost effective, but milder, oxidant. The downside to using oxygen is formation of radicals which can lead to repolymerization of the monomers, which decreases yields of aromatic monomers.[3]

A plethora of studies have been done on the topic of catalytic oxidative depolymerization of technical lignins, with many being done in batch reactors[27] in alkaline aqueous media[3]. Vanillin yields of up to 7 wt% have been reported when vanadium and copper have been used together as a bimetallic homogeneous catalyst for oxidative depolymerization of Kraft lignin in alkaline media[25]. When using a heterogeneous copper-vanadium catalyst, vanillin yields up to 6 wt% were achieved[15]. Other reaction media such as methanol[28], ionic liquids[1] and γ-valerolactone[29] have also been explored with varying monomeric yields depending on process conditions and pre-treatment of the lignin feedstock.

Fewer studies have been done on continuous depolymerization systems, although continuous flow systems present several advantages compared with batch systems. In a continuous flow system, the residence time is shorter than in a batch system, which decreases the energy demand of the process. The preheating and cooling down of the feed and product stream are also shorter which both lowers the energy demand and minimises the risk of unwanted side reactions occurring during the heat-up and cool-down. The challenges of using continuous flow systems are similar to the challenges of using batch reactors, with the heterogeneity and robust bonds of technical lignin being the main challenges. There might however be additional problems with solid deposits in the tubing causing clogging of the system if plug flow reactors (PFRs) are used. These problems could however be mitigated through using continuous stirred-tank reactors (CSTRs), which could enable better control of the system. Lastly, continuous flow systems enable for easier energy recovery, and are an important step in taking the process from a laboratory scale towards industrial applications.[27]

1.6.2.1 Biphasic oxidative depolymerization (BPD)

BPD is a novel approach to oxidative depolymerization, which combines lignin depolymerization in an acidic phase with the extraction of the products in an organic phase. Oxygen is used as an oxidant, and 1-octanol is used as the organic phase. The purpose of adding the organic layer is to protect the monomers from over oxidation and preventing them from repolymerization, thus increasing yields. Another advantage of the biphasic system is the elimination of an extraction step in the process if it were to be scaled up, which could save investment and operating costs. Similar methods have been explored for valorisation of cellulose and hemicellulose, but the concept was recently suggested for lignin valorisation. It has proven to be an effective method for achieving high yields of aromatic monomers such as vanillin when combined with $FeCl_3$ as a homogeneous catalyst. The process has only been investigated at a small scale, with low lignin loading (1 mg/mL) and a high ratio of catalyst to lignin.[7, 8]

1.6.3 Biological conversion of depolymerization products

The products from oxidative lignin depolymerization have a wide variety of applications either directly as food flavouring, or as precursors to pharmaceuticals or plastics. One way of further processing the depolymerization products is through biological conversion, where the products are fed to modified bacteria which convert the monoaromatic compounds to muconic acid. Muconic acid is a highly functionalised aliphatic diacid, commonly used to produce different plastics, such as nylon-6,6[30]. Presently, muconic acid is produced from fossil-derived adipic acid. Lignin-derived muconic acid could lower the emissions of CO_2 equivalents by up to 78% compared to the fossil-based production[13].

1.7 Industrial lignin depolymerization

Historically, lignin has been widely used as a feedstock for vanillin production, but, as previously mentioned, Borregaard is currently the only industrial producer of aromatic fine chemicals from lignin[19]. The process uses copper salts as catalysts, and yields around 7 wt-% of lignin from the softwood lignosulfonate used as feedstock in the process[31]. Thus, there is no commercial production of aromatic fine chemicals derived from kraft lignin, even though it represents the vast majority of the lignin produced from pulping plants worldwide.

For a lignin-valorisation process to be economically and environmentally feasible, there are a few criteria that should be considered before scaling up. First, since the feedstock is abundant and inexpensive and the products much more valuable, the process should be able to have a high throughput of technical lignin. Furthermore, the cost and recyclability of the catalysts should also be considered, the cost of solvents and solvent loss through evaporation and the deactivation and inhibition of catalyst and substrates should be kept to a minimum. Expensive stoichiometric reagents should also be avoided and the environmental impact of the waste materials should be considered[19]. It could also be an advantage to design the process so that it could be integrated with a pulp mill, so that for example a black liquor stream could be taken directly into a depolymerization process[5]. This would save on both costs and potential emissions caused by transportation of the lignin from the pulp mill to the depolymerization plant and save costs from precipitating and drying the kraft lignin before the depolymerization.

A techno-economic evaluation of a oxidative Kraft lignin depolymerisation process by Abdelaziz et al.[5], based on experimental data shows that such a process is economically viable at large scale. Still, further research is needed to improve yields to make the process feasible to scale up to industrial production volumes. Another simulation of a lignin valorisation process by Plesu Popescu et al[32]. investigated the use of different organic solvents for extracting the vanillin produced in the depolymerization process. The authors found that although ethyl acetate is widely used to extract the aromatic monomers, other organic solvents such as hexanol could be better options in terms of solvent loss and elimination of process steps

2 Materials and methods

Due to inconsistent particle size in the Indulin AT, the lignin was sieved and fractionated into different particle sizes: 200–500 µm, 125–200 µm, 90–125 µm, 45–90 µm and <45 µm. Each fraction of the lignin was then weighed. For all BPD experiments, and for the extraction of the lignin in organic solvents, only the smallest particle size was used.

2.1.1 BPD

The depolymerization of lignin was done using the organic synthesis mode in a Biotage Initiator microwave reactor at pH 1 and a lignin loading of 1 mg/mL in the aqueous phase. For the homogeneous catalyst screening, the experiments were carried out at T = 170 ° C and τ = 20 minutes with a catalyst loading of 10 mM. 0.5 ml of 4 mg/mL Indulin AT dissolved in 0.02 M sodium hydroxide (Sigma) was loaded together with 0.5 mL of 40 mM aqueous catalyst solution and 1 mL of 0.2 M HCl solution (prepared from concentrated HCl, 37% from Fluka) and 2 mL of octanol (Riedel de Haën) into 10 mL reaction vials with a magnetic stirrer, which were then sealed.

For the experiments using heterogeneous catalysts, the catalyst loading was calculated to equate 10 mM metal (10–12.2 mg/vial depending on the catalyst used) and 0.5 mL of LC/MS-grade water (Fluka) was added instead of aqueous catalyst solution. The catalyst calculations were done according to equations 1-2 and the catalyst loading for each type is presented in Table 1. The octanol was washed three times with 0.1 M HCl and then three times with LC/MS-grade water. The sealed mixtures were then saturated with Ar (≥99.98%) or O_2 (≥99.998%) for 15 minutes while stirring. To get a baseline of the oxidative depolymerization reaction, one reaction was done using no catalyst and one with catalyst support only. All reactions were performed in duplicates. Assuming that the average monomeric unit in lignin has a molecular weight of 164 g/mol[5], the homogeneous catalyst to lignin ratio was 10:6 mol/mol, and in the case of heterogeneous catalysts it was 5-6.1:1 w/w.

$$M_{avg} = \frac{n_i \cdot M_i + n_j \cdot M_j}{n_i + n_j} \tag{1}$$

$$m_{cat} = \frac{m_{metal}}{metal\ loading} = \frac{V_{aq} \cdot c_{cat} \cdot M_{avg}}{metal\ loading} = \frac{2 \cdot 10^{-3}\ l \cdot 10\ \cdot 10^{-3}\ M \cdot M_{avg}}{0.1} \tag{2}$$

Where M_{avg} is the average molecular weight of the metal phase in the catalysts with the ratio n_i:n_j between metal i and metal j where M_i and M_j are the molar masses of these compounds (g/mol). The amount of catalyst added to each vial is denoted m_{cat} (g), V_{aq} is the volume of the aqueous phase in the system (2 ml) and c_{metal} is the desired metal concentration in the aqueous phase (10 mM).

Table 1: Catalyst loading in the vials for each type of catalyst.

Catalyst	Mass added to vial (mg)
ZrO_2 support only	10
2:1 Fe:Cu	11.7
3:1 Fe:Cu	11.6
2:1 Fe:Co	11.3
3:1 Fe:Co	11.3
Fe	11.2
1:1 Cu:Co	12.2

The salts used for the catalyst screening were Iron(II) chloride tetrahydrate (Sigma), Iron(III) chloride hexahydrate, Iron(III) nitrate nonahydrate, Cobalt(II) chloride hexahydrate, Cobalt(II) nitrate hexahydratel copper(II) acetate monohydrate (Fluka), Cobalt(II) acetate tetrahydrate (Alfa Aesar), Cobalt(II) sulphate heptahydrate (Thermo), Copper(II) chloride (Strem chemicals), Copper(II) nitrate trihydrate (Fluorochem), Copper(II) sulphate pentahydrate (Aldrich), Iron(II) sulphate heptahydrate (ITW reagents) and Iron(III) sulphate pentahydrate (Riedel de Haen).

2.1.2 Preparation of heterogeneous catalysts

Five of the catalysts were prepared from ZrO_2 (Alfa Aesar) using the incipient wetness method. The water uptake of the support was first measured to be 0.4 ml/g. Five of the catalysts were prepared using the nitrate salts of iron, cobalt and copper (Chemisphere Ltd), aiming at 10% by weight of the reduced metals on the catalyst support. Due to the low water uptake, the catalysts were prepared in two steps, with impregnation in between. Based on the high presence of crystal water in the nitrates (9 for iron nitrate, and 6 for both copper and cobalt) and the low water uptake of the materials, the nitrate salts were weighed in and heated to approximately 60 °C, with a few drops of water. When adding more than one metal, the salts were added together in a mix. The molten nitrate salts were added to a pre-determined amount of ZrO_2 catalyst support, preheated to 60 °C. The catalysts were put in a furnace and calcined. The temperature program was 120 °C /h to 120 °C where the catalysts were dried for 4 h. The temperature was then increased by 120 C/h to 500 °C, where the catalyst was calcined for 4 h. The temperature program was the same for both calcinations.

The first catalyst was 10% iron on zirconia, to which 10 g of catalyst support was weighed in and 1.1 g of iron added. This means 7.96 g of iron nitrate was added, equally distributed in two impregnations.

The second catalyst was 10% Iron and copper in a ratio of 2:1 by weight. To 10 g of catalyst support 0.73 g of iron and 0.37 g of copper was added. This is equivalent to 5.26 g of iron nitrate and 4.76 g of copper nitrate.

The third catalyst was 10% Iron and copper in a ratio of 3:1 by weight. To 10 g of catalyst support 0.83 g of iron and 0.28 g of copper was added. This is equivalent to 5.96 g of iron nitrate and 3.58 g of copper nitrate.

The fourth catalyst was 10% Iron and cobalt in a ratio of 2:1 by weight. To 10 g of catalyst support 0.73 g of iron and 0.37 g of copper was added. This is equivalent to 5.26 g of iron nitrate and 1.80 g of cobalt nitrate.

The fifth catalyst was 10% Iron and cobalt in a ratio of 3:1 by weight. To 10 g of catalyst support 0.83 g of iron and 0.28 g of cobalt was added. This is equivalent to 5.96 g of iron nitrate and 1.36 g of cobalt nitrate.

The sixth catalyst was prepared using the same method for impregnation and the same ZrO_2 support, but after each impregnation they were dried for 4 hours at 100 °C and then calcined at 450 °C for 8 hours. Copper acetate and cobalt chloride hexahydrate were used, with 10% copper and cobalt in a ratio of 1:1. To 14 g of catalyst support, 0.7 g of copper and 0.7 g of cobalt was added. This is the equivalent of 2.88 g cobalt chloride hexahydrate and 2.13 g of copper acetate.

2.1.3 Chemical analysis

2.1.3.1 BPD product pool

The octanol phase and the aqueous phase were separated and filtered through a 0.22 μm filter. The samples were stored at -20 °C. For analysis in LC-MS, the octanol phase samples were thawed and then transferred to chromatography vials and diluted 10 times in methanol with 10 μM tryptophan-d5 (Cambridge Isotope Laboratories) as the internal standard.

Chromatographic separation was performed using ultra-high performance liquid chromatography (UHPLC, Thermo Scientific, Dionex Ultimate 3000 series RS), which was then followed by high resolution mass spectrometry (HRMS) with a Q Exactive hybrid quadropole-orbitrap mass spectrometer (Thermo Scientific), negative mode electrospray ionization, full scan MS1. For the initial analysis of the samples, the column and precolumn used were Aquity UPLC BEH C18 columns (50mm x 2.1 mm, particle size 1.7 μm). The flow rate was set to 0.5 ml/min, the column temperature was 50 °C and the sample injection volume 1 μL. A program using mobile phase A (1 vol-% methanol, 1 vol-% acetonitrile and 0.02 vol-% formic acid in HPLC-grade water) and mobile phase B (100 % methanol) was used. At 0-0.8 min the mobile phase was 1%B, between 0.8-1.8 min B increased from 1% to 99%, at 1.8-3min 99% B, between 3-

3.050 min B decreased to 1% and lastly between 3.050-3.6min 1% B. All solvents were purchased from Fluka. The data from this analysis was used to compare the different catalysts in terms of reaction products and abundance of different compounds.

After analysing the data from the initial LC-MS, samples were selected for quantification of products. These were then re-analysed using a longer method with a different column and precolumn from Thermo Scientific Sccuore RP-MS (150mm x 2.1 mm, particle size 2.6 µm). The flow rate was set to 0.7 ml/min, the column temperature was 50 °C and the sample injection volume 1 µL. A program using mobile phase A (1 vol-% methanol, 1 vol-% acetonitrile and 0.02 vol-% formic acid in HPLC-grade water) and mobile phase B (100 % methanol) was used. At 0-0.1 min the mobile phase was 1%B, between 1-6 min B increased from 1% to 99%, at 6-8 min 99% B, between 8-2 min B decreased to 1% and lastly between 8-10min 1% B.

The raw mass data files were collected in duplicate and were imported into Compound discoverer 3.3 software from Thermo Scientific (Switzerland) and processed with standard settings. The "Fill Gaps" function was used to check chromatographic peaks detected in only one of the input files. The composition was predicted based on isotopic patterns and exact mass. The predicted compositions were searched for in the ChemSpider compound library to identify compounds. Hierarchical cluster analyses were performed to identify differences and similarities between the different catalysts with regards to their respective product pools. This method creates clusters through a sequential pairing of clusters, variables, or clusters and variables. At each step, the clusters and unclustered variables are combined in pairs, and the pair with the highest intercorrelation is chosen as a new cluster[33].

2.1.3.2 Quantification of monomers

Yields were calculated based on equations 3-5 based on the masses of monomers produced calculated from concentrations and peak areas measured in the UHPLC-HRMS. An external calibration curve for vanillin and 5-nitrovanillin (0.05–10 µg/mL, R^2>0.99, $\sigma < 5\%$) was used to determine the concentrations of said compounds. The calibration curve was normalised to an internal standard and corrected for the dilution of the BPD samples. The vanillin and 5-nitrovanillin peak areas measured in the selected samples using the longer UHPLC-method were recalculated to yields on a lignin mass basis.

$$c_m = \frac{A_m/A_{IS}}{RF}\frac{C_{IS}}{df} \tag{3}$$

$$m_m = c_m \cdot V_{oct} \tag{4}$$

$$Y_m = \frac{m_m}{m_{lignin}} \cdot 100\% \tag{5}$$

Where c_m is the monomer concentration (µg/ml), A_m is the monomer peak area, A_{IS} is the internal standard peak area, c_{IS} the internal standard concentration (µM), df is the dilution factor

(1/10), m_m is the monomer mass (µg), V_{oct} is the volume of the octanol phase (2 ml), Y_m is the monomer yield (wt%) and m_{lignin} is the lignin mass (µg).

2.1.3.3 Catalyst characterization

To determine the specific surface area of the catalysts and the catalyst support, N_2 physisorption was done on a Quantachrome Autosorb AS1 instrument. The samples were outgassed at 250 degrees for 3 hours before measurements and the specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method. Powder X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance diffractometer to determine the crystalline phase structure of the catalysts. Cu Kα radiation with a wavelength of 1.54 nm was used with a 2θ range of 20°-80° with a step size of 0.02 and a scanning speed of 0.4° per minute.

3 Results and discussion

In the following sections, the results from the catalyst screening are presented. Monomeric yields and product pools for the different catalysts are compared and discussed, and suggestions for future work are given.

3.1 Vanillin production

Figure 2 shows that the highest vanillin areas for each metal in the homogeneous catalyst screening were found in the samples using chloride salts in oxygen atmosphere. Therefore, the samples from experiments using iron(III) chloride, iron(II) chloride, copper(II) chloride and cobalt(II) chloride in oxygen atmosphere were selected for vanillin quantification.

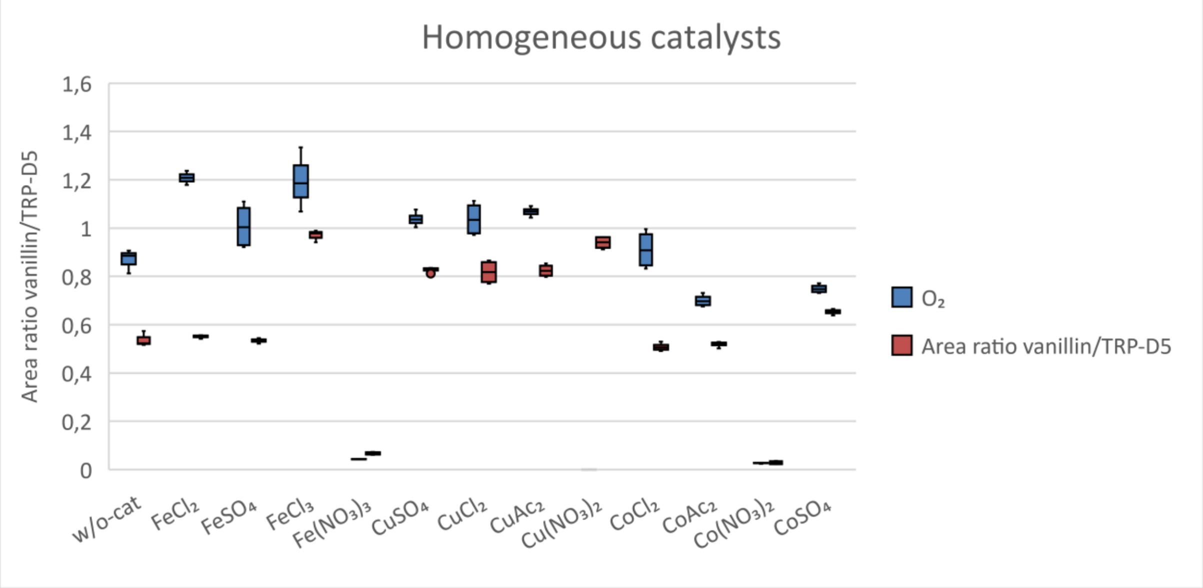

Figure 2: Area ratios of vanillin/internal standard for homogeneous catalysts under argon and oxygen atmospheres.

When looking at the area ratio of vanillin/internal standard for the different homogeneous catalysts, presented in Figure 2, most catalysts achieve higher ratios than the experiment where no catalyst is used. The exceptions to this are cobalt sulphate and cobalt acetate, along with most experiments using nitrate salts. When comparing experiments using oxygen atmosphere and argon atmosphere, it is apparent that the oxygen favours vanillin production, except when using nitrate salts, and does indeed act as an oxidant in the depolymerization.

In argon atmosphere, the iron(II) catalysts produce comparable amounts of lignin as when using no catalyst. In oxygen atmosphere, the catalysts produce more vanillin than the experiments without catalysts, indicating that the oxygen oxidises the Fe^{2+} ions into Fe^{3+} before the oxidative depolymerization can commence.

The vanillin was also quantified in all samples using heterogeneous catalysts in oxygen atmosphere, as there was little difference between the vanillin areas among the heterogeneous catalysts, as shown in Figure 3.

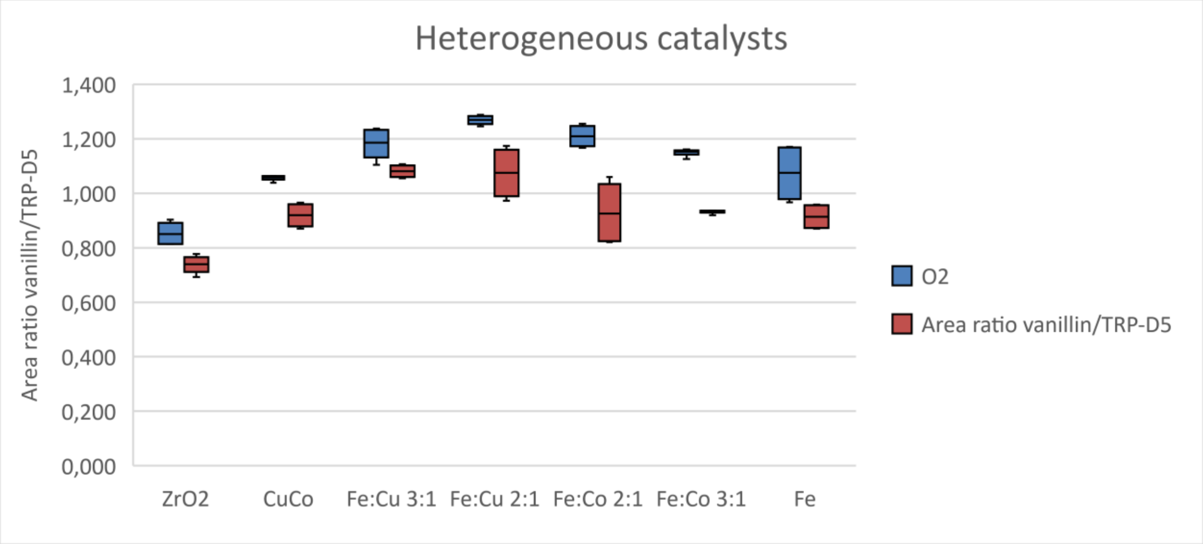

Figure 3: Area ratios of vanillin/internal standard for heterogeneous catalysts in argon and oxygen atmosphere.

The area ratios for the heterogeneous catalysts are all similar, especially the bimetallic iron-containing catalysts. It is difficult to determine catalyst is the best performing, as the error bars for some of the experiments cover a larger range and overlap with other catalysts. It is however clear that all catalysts perform better than when using the ZrO_2 support only.

3.1.1 Yields

Vanillin was the most abundant monomer that could be identified in the product pool from the homogeneous and heterogeneous catalyst screening. Since the other monomers were in concentrations too low or not possible to identify, vanillin was the only product chosen for quantification (calibration curve presented in Appendix A). Vanillin yields for the selected samples are presented in Figure 4. Among the homogeneous catalysts, it is clear that iron(II) and iron(III) chloride are best performing catalysts with yields of 1.1 wt-% and 1 wt-% (± standard deviation) respectively. However, there is no statistically significant difference between the two. Copper chloride is the second best performing homogeneous catalyst with a yield of 0.9 wt-%, followed by cobalt chloride at 0.6 wt%. Compared to the baseline yield of 0.4 wt% when using no catalyst, the use of catalysts favour vanillin production in the system with an increased vanillin yield of up to 175%.

As for the heterogeneous catalysts, it is also clear that the catalysts promote vanillin production in the system, as the yields for all heterogeneous catalysts are higher than when using the ZrO_2 support only. The catalyst support does however seem to have some influence on the depolymerization, as the vanillin yield is higher when using the support than when using no catalyst at all. There is no statistically significant difference between the yields for the heterogeneous catalysts, as the errors for some of these experiments were quite large due to poor reproducibility. Therefore, no single heterogeneous catalyst can be said to be performing better than the others. Yields from the heterogeneous catalysts are comparable to the yields from the homogeneous iron-based catalysts, with the highest yields being just below 1 wt-%.

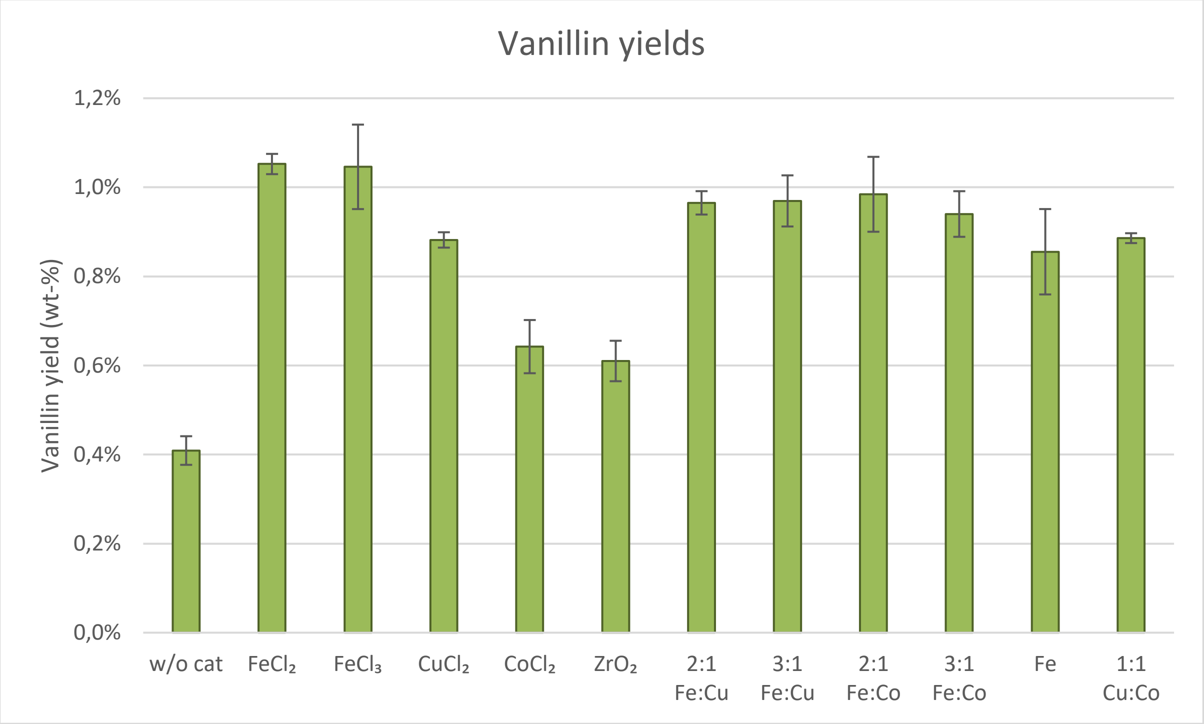

Figure 4: Vanillin yields for the selected catalysts.

3.2 Product analysis

In the following section, the products from the BPD with different catalysts are compared and discussed. First, the homogeneous catalysts are compared, followed by the heterogeneous catalysts.

3.2.1 Homogeneous catalysts

When further investigating the product pool from the experiments using nitrate salts as homogeneous catalysts, aromatic species with nitrate groups were identified. The most abundant of these (with regards to peak area) was identified as 5-nitrovanillin. The highest yield of 5-nitrovanillin was found in samples using copper nitrate in copper oxygen atmosphere and was calculated to 0.6 wt% (calibration curve presented in Appendix A).

The analysis of the product pool for the homogeneous catalysts mainly focused on four categories of species: aromatic monomers, nitrated aromatics, dimers and diacids. In the samples from the homogeneous catalyst screening, 20 compounds were identified as belonging to one of these categories. Three of these compounds were possible to verify through confirming retention times with standard solutions: 5-nitrovanillin, vanillin and divanillin. Of the 20 compounds belonging to these categories, 12 were only present in the samples where nitrate salts had been used. These compounds were either nitrated aromatics or diacids, neither of which were found in the other samples. The 8 compounds belonging either to the category aromatics or dimers were on the other hand only abundant in the samples which were not using nitrates. These compounds are presented in Table 2 going from the highest peak area to the lowest. The compound names marked with * are suggestions based on results from a ChemSpider search and have not been confirmed through injection of standards containing the compounds to check for retention time.

*Table 2: Compounds found in samples with homogeneous, non-nitrate catalysts. Compound names marked with * are suggestions based on matches in the ChemSpider compound library.*

Category	Sum formula	RT (min)	Name
Aromatic monomer	$C_8H_8O_3$	1.867	Vanillin
Aromatic monomer	$C_9H_{10}O_5$	1.652	Vanillyl mandelic acid*
Dimer	$C_{16}H_{14}O_6$	2.023	Divanillin
Aromatic monomer	$C_{10}H_{12}O_5$	1.825	-
Aromatic monomer	$C_9H_{10}O_4$	1.744	Homovanillic acid*
Aromatic monomer	$C_{10}H_6O_5$	1.677	-
Aromatic monomer	$C_8H_6O_3$	1.775	-
Dimer	$C_{15}H_{14}O_2$	2.259	-

The diacids and nitrated aromatics found are presented in Table 3, going from the highest peak area to the lowest. The compound names marked with * are suggestions based on results from a ChemSpider search and have not been confirmed through injection of standards containing the compounds to check for retention time.

*Table 3: Compounds found in samples with homogeneous nitrate catalysts. Compound names marked with * are suggestions based on matches in the ChemSpider compound library.*

Category	Sum formula	RT (min)	Name
Diacid	$C_{12}H_{20}O_4$	2.305	Traumatic acid*
Diacid	$C_{10}H_{18}O_4$	3.013	Sebacic acid*
Nitrated aromatic	$C_8H_7NO_5$	1.970	5-nitrovanillin
Nitrated aromatic	$C_7H_6N_2O_6$	2.226	4,6-Dinitroguaiacol*
Nitrated aromatic	$C_8H_7NO_6$	1.962	5-nitrovanillic acid*
Nitrated aromatic	$C_6H_5NO_3$	1.967	Nitrophenol*
Nitrated aromatic	$C_7H_7NO_4$	1.994	2-methoxy-4-nitrophenol*
Diacid	$C_{16}H_{30}O_5$	2.365	7/8-hydroxydecanedioic acid*
Nitrated aromatic	$C_8H_6N_2O_4$	2.026	-
Nitrated aromatic	$C_8H_9NO_3$	2.151	-
Nitrated aromatic	$C_7H_6N_2O_5$	1.875	-
Nitrated aromatic	$C_{10}H_{11}NO_7$	1.922	-

The results of the hierarchical cluster analysis for the homogeneous catalysts are summarised in Figure 5. The clusters separated the separates the nitrate salts from the rest of the catalysts into one cluster, and the rest of the catalysts are divided into sub-clusters. The product pool is similar for all nitrate salts, consisting of the compounds presented in Table 3. All copper catalysts are clustered together and produce an even distribution of all aromatic monomers identified in Table 2. Cobalt acetate, cobalt sulphate and samples with no catalyst are clustered together, producing mostly homovanillic acid. Cobalt chloride and iron sulphate produce less vanillin than copper salts and iron chlorides, producing more dimers instead. The iron chlorides have a high selectivity for vanillin and produce very little of the other products in Table 2. The full hierarchical cluster analysis is presented in Appendix B.

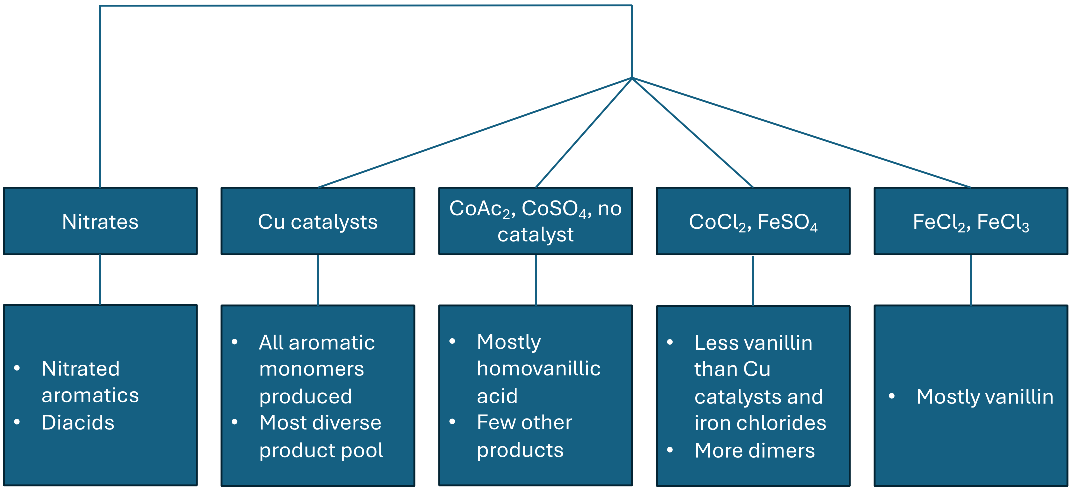

Figure 5: Summary of hierarchical cluster analysis for homogeneous catalysts.

3.2.2 Heterogeneous catalysts

The product pool from the heterogeneous catalyst screening is less diverse than from the homogeneous catalyst screening. The products could be divided into two different categories: aromatic monomers and dimers. Nine compounds were found, one of which was divanillin and the rest were aromatic monomers. The compound names marked with * are suggestions based on results from a ChemSpider search and have not been confirmed through injection of standards containing the compounds to check for retention time. These compounds are presented in Table 4 going from the highest peak area to the lowest.

*Table 4: Compounds found in samples with heterogeneous catalysts. Compound names marked with * are suggestions based on matches in the ChemSpider compound library.*

Category	Sum formula	RT (min)	Name
Aromatic monomer	$C_9H_8O_5$	1.969	-
Aromatic monomer	$C_8H_8O_3$	1.851	Vanillin
Aromatic monomer	$C_9H_8O_5$	2.244	-
Aromatic monomer	$C_7H_6O_2$	1.784	4-Hydroxybenzaldehyde*
Aromatic monomer	$C_9H_8O_6$	2.266	-
Aromatic monomer	$C_{10}H_{10}O_4$	1.965	-
Aromatic monomer	$C_9H_{10}O_4$	1.750	Homovanillic acid*
Dimer	$C_{16}H_{14}O_6$	2.004	Divanillin
Aromatic monomer	$C_7H_6O_3$	1.662	4-hydroxybenzoic acid*

A summary of the hierarchical cluster analysis of the heterogeneous catalysts is presented in Figure 6. Three main clusters were identified, one for the samples with no catalyst, one for the samples with ZrO_2 support and one for the catalysts. The cluster with all catalysts is separated into three sub-clusters with different product pools. The copper-cobalt catalyst produces the least amount of vanillin but has two products in common with the iron-copper catalysts. The iron-copper catalysts produce more vanillin than the copper-cobalt catalysts and slightly less divanillin than all other catalysts. The iron-cobalt and iron only catalysts have a less diverse product pool than the copper-based catalysts. The zirconia support has a different product pool than the samples with no catalysts, indicating that the support has some activity in the reaction. The full hierarchical clusters are presented in Appendix B.

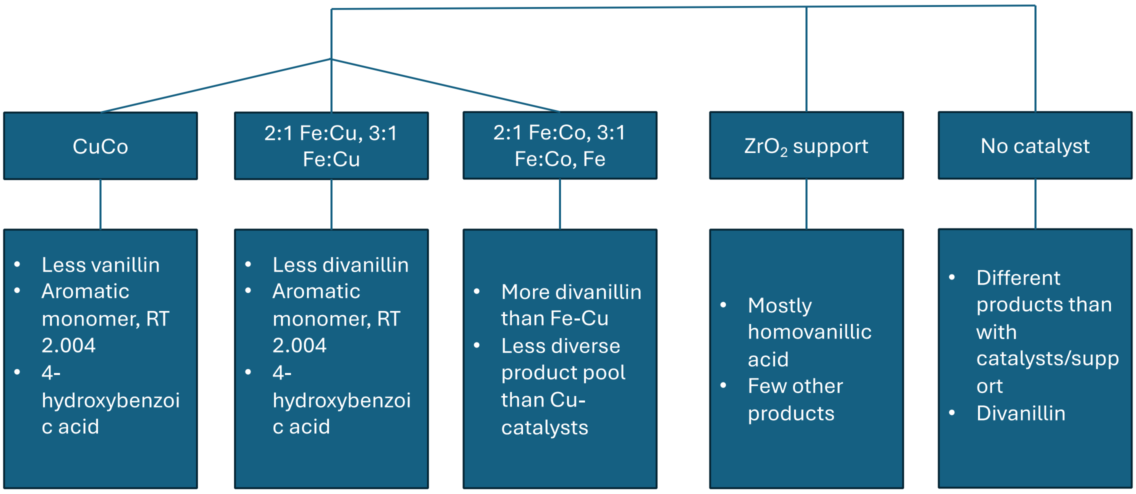

Figure 6: Summary of hierarchical cluster analysis for heterogeneous catalysts.

3.3 Catalyst characterization

The specific surface areas of the catalyst support and all catalysts are presented in Table 5. The surface areas are all similar and the untreated support has the highest surface area of 54.4 m^2/g and the 2:1 Fe:Cu catalyst had the lowest measured surface area of 46.6 m^2/g. The surface areas were measured once for each catalyst.

Table 5: Specific surface area for the heterogeneous catalysts.

Catalyst	**Surface area**
Support only, ZrO_2	*54.4 m^2/g*
Fe	*46.5 m^2/g*
2:1 Fe:Cu	*46.4 m^2/g*
3:1 Fe:Cu	*51.3 m^2/g*
2:1 Fe:Co	*48.9 m^2/g*
3:1 Fe:Co	*48.8 m^2/g*
1:1 Cu:Co	*47.5 m^2/g*

The XRD-spectra (presented in Appendix C) showed no difference in the metallic phases between the catalysts using the same metals at different ratios. The phase in the copper-cobalt catalysts was a solid solution of the two metals, and the catalyst containing pure iron had iron(III) oxide with a hexagonal structure. For the iron-cobalt catalysts, the metals formed a solid solution of iron and copper with a cubic structure, and for iron-copper catalysts there was a mixture of copper oxide and cubic iron oxide and a solid solution of the two metals.

3.4 Catalyst performance

Based on the results from the catalyst screening, the iron-based homogeneous catalysts are the best performing, followed by the bimetallic iron-containing heterogeneous catalysts. The vanillin yields are lower than a previous study done using the BPD-system[7] and other studies on alkaline oxidative depolymerization of Kraft lignin using both homogeneous and heterogeneous catalysts[15, 25, 34]. The reason for the difference in yields between this study and previous BPD studies could be that a longer reaction time (40 minutes) was used in the previous experiments where yields up to 7% were achieved, or differences between the lignins making the lignin used in this work more difficult to depolymerise. The yields from the best performing heterogeneous catalysts are comparable to the yields from the best performing homogeneous catalysts, as the differences are not statistically significant. This is surprising, as heterogeneous catalysts tend to be less active than homogeneous catalysts[12]. Since the best performing catalysts all have yields around 1 wt%, it could be an indication that the reaction is limited by something other than the catalysts. Since oxygen is not continuously supplied during the reaction, and since the reaction vials were not pressurised, it is possible that the oxygen is depleted before the lignin is fully converted.

It could also be due to the high catalyst loading in the system, as the catalyst to lignin ratio in the heterogeneous experiments is roughly 5-6.1:1 w/w. This high ratio was used due to wanting to keep the concentration of metal inside the reaction comparable to the homogeneous experiments at 10 mM. Assuming an average monomeric molecular weight of 164 g/mol[5], this gives a metal to lignin ratio of 10:6 mol/mol. As there is more catalyst than lignin within the BPD system, there is likely an abundance of active sites on the catalysts that can aid in the depolymerization and contribute to the high yields. The similar yields could also be due to leaching of the metals from the heterogeneous catalysts, turning it into a homogeneous catalytic system. However, due to the very high catalyst loading, it cannot be said with complete certainty that the process is catalytic.

Moreover, the homogeneous samples that were quantified were stored about a month longer at -20 degrees, than the heterogeneous samples before they were analysed. It was assumed that the samples would be stable for this amount of time, but it was never fully investigated. It is unlikely that the vanillin was degraded due to long storage, as it has been shown that depolymerization products are stable in long term storage at 4 °C[35].

The relatively high yields from the heterogeneous catalysts could also be due to the combination of iron with either copper or cobalt. These bimetallic combinations were not tested as homogeneous catalysts, due to the risk of precipitation of salts that could cause overheating in the microwave reactor. To determine if it is the high catalyst loading or the bimetallic combinations that are the cause for the high yields, the metallic combinations would have to be tested homogeneously to compare with the iron chlorides. A heterogeneous iron only catalyst was screened, but due to poor reproducibility between the duplicates, it is difficult to say how its performance compares to the bimetallic iron containing catalysts. Iron-based catalysts do however seem to favour higher yields of vanillin in both homogeneous and heterogeneous tests.

The copper and cobalt-based catalyst performed worse in the homogeneous catalyst screening, and the heterogeneous copper-cobalt catalyst performed worse than the iron-containing bimetallic catalysts. From the hierarchical cluster analysis, showed in Figures 5-7, it is evident that the copper and cobalt chlorides have a more diverse product pool than the iron chlorides catalysts, which are more selective towards vanillin. This does not necessarily mean that these catalysts are bad at producing vanillin from lignin, it could also be a sign that they are producing vanillin faster than the iron-based catalysts and that it is transformed into other compounds through unwanted side reactions. This could be investigated through testing different reaction times and see how the vanillin yields are affected for the different catalysts. The lignin conversion could also be monitored through size exclusion chromatography, which gives information on how the molecular weight of the products are affected during the process. The lower the average molecular weight, the more lignin has been converted[36].

The environmental effects and health implications of each catalyst should also be considered. Both copper and cobalt are very toxic to aquatic life with long lasting effects,[37, 38] and cobalt is suspected to cause cancer, damage fertility, and cause genetic defects[38]. Iron on the other hand does not have these effects on the environment and human health[39].

3.4.1 Heterogeneous catalyst properties

The XRD-spectra (presented in Appendix B) showed no difference in the metal phases between the 2:1 iron-copper catalyst and the 3:1 iron-copper catalyst, or the 2:1 iron-cobalt catalyst and the 3:1 iron-cobalt catalyst. The different metallic ratios did therefore not affect the metal phase in the catalysts. As there is no statistically significant difference in the vanillin yields between any of the iron-copper and iron-cobalt catalysts, the metallic ratio also does not affect the depolymerization process. The specific surface area of the catalysts does not seem to affect the product yields significantly, as the catalyst with the lowest measured surface areas (2:1 Fe:Cu, 46.4 m^2/g) still achieves among the highest yields. However, it is once again difficult to draw any clear conclusions due to issues with reproducibility, causing large errors for some calculated yields. As previously mentioned, the iron content seems to be the most important factor for achieving higher vanillin yields and selectivity in this process.

3.4.2 Reproducibility of heterogeneous experiments

The issue with reproducibility in the heterogeneous experiments makes it more difficult to evaluate the performance of the individual catalysts. It was observed that the catalysts were crushed by the magnetic stirrer during the gas purging step before the reaction and during the reaction itself. In some cases, the catalysts appeared to be evenly distributed in the reaction mixture, but in other cases the catalysts were agglomerated at the bottom of the vial. This crushing could be a contributing factor to the variation in vanillin production between the duplicates, however the effects of the reaction on the catalysts were not evaluated through any measurements. To protect the catalysts from being crushed, a cage containing the catalysts could be constructed which could keep them away from the magnetic stirrer.

3.4.3 Nitrated depolymerization products

The fact that nitrogen containing compounds are produced when using nitrate salts in the BPD system means that the salts are not catalysts but rather reactants. This is rather surprising, as none of the other anions from the other types of salts have incorporated into the products. In a study by Zhang et al.[28], iron(III) chloride was used as a catalyst for lignin depolymerization together with sodium nitrate as a co-catalyst. This is similar to when iron(III) nitrate is used in the BPD system. The idea was that when the Fe^{3+} oxidises the lignin, it is reduced to Fe^{2+}, and to regenerate the iron back to Fe^{3+} the nitrate ions would oxidize the iron and turn into nitrite ions. The nitrite ions would in turn be oxidized back into nitrate ions by the oxygen present in the reactor. No nitrated compounds were reported as reaction products, but total monomeric yields of up to 5.2 wt-% were reported, where the main products were vanillic acid, vanillin and syringic acid. The differences between the BPD system and the system used by Zhang et al. are mainly the reaction media, which was methanol or water instead of hydrochloric acid (methanol achieved highest yields) and the lignin and catalyst loading. 10 mg/mL lignin, around 0.15 mM $FeCl_3$ and 0.30 mM $NaNO_3$ was used in the system, which is a much higher lignin loading and much lower catalyst loading. The catalyst to lignin ratio is thus very different from the BPD system, and there are much less nitrate ions available for production of nitrated aromatic monomers.

Nitrated lignin products have however been shown to be produced through nitric acid pulping[40, 41] and through lignin depolymerization using fuming nitric acid under ambient conditions[42].In these cases, however, the goal is not to produce high-value aromatic monomers. 5-nitrovanillin, which is the most abundant nitrated aromatic produced in the BPD-system, can be used as a precursor in pharmaceutical production[43, 44] and as a yellow colouring agent in hair dye[45]. There are different ways of synthesizing 5-nitrovanillin from vanillin[46], but no sources have been found where it has been identified as a reaction product from lignin depolymerization.

3.5 Future Work

Although the BPD process has achieved high yields of aromatic monomers historically[7], the system has only been investigated at a very small laboratory scale, with a very low substrate loading. In this study, the highest yields are still relatively low when compared to other studies performed in systems without two liquid phases[3, 20, 28]. The system needs to be further studied, possibly through a time and temperature optimization with one of the better performing catalysts to determine the optimal parameters to maximise yields. This could be done in a larger batch reactor with the possibility of increasing the oxygen partial pressure, or constant oxygen supply to avoid limiting the depolymerization reaction. The system also needs to be investigated at a larger scale, with a higher lignin loading to evaluate how it performs in conditions closer to industrial production. This could be done in a continuous setup, as there are several advantages to performing lignin depolymerization in continuous flow systems compared to corresponding batch processes[27].

The hydrochloric acid in the aqueous phase could decrease the performance of the heterogeneous catalysts, as chloride ions are a known catalyst poison, meaning that they block active sites on the catalysts and thus decrease the catalytic activity[26]. The effect this has on the heterogeneous catalysts has not been evaluated, but since the vanillin yields were comparable to the best performing homogeneous catalysts it does not seem to have a significant effect in this system. However, as previously mentioned the catalyst to lignin ratio is very high, and thus there might still be plenty of active sites that can participate in the reaction compared to the amount of lignin present. If the catalyst to lignin ratio would decrease, the effect of the hydrochloric acid could be more pronounced, and therefore it could be worth exploring other options such as sulfuric acid, as sulphate ions are less toxic to the catalysts than chloride ions[26]. The metal loading of the catalysts could also have been confirmed through for example Inductively Coupled Plasma Optical Emission spectroscopy (ICP/OES) measurements. Leaching of metal from the heterogeneous catalysts could also be monitored through ICP/OES measurements of the octanol and aqueous phases after the reactions[47]. If there is significant metal leaching, the process is more comparable to heterogeneous catalysis, and the purpose of the heterogeneous catalysts is defeated.

To get a better idea of how the system could perform in industrial conditions, the stability of the heterogeneous catalysts in the reaction should also be evaluated. It was noted that the catalysts were crushed by the magnetic stirrer to a finer particle size, but things such as surface area changes or phase changes in the metal were not investigated due to the small amounts of catalysts used in each batch. The reactions could be done in larger volumes to increase the amount of catalyst used in each batch. The catalyst degradation could also be evaluated through using the same catalysts several times and monitor the monomeric yields after each cycle. This information could then be used to optimise the catalysts to improve stability, if needed, as one of the advantages of heterogeneous catalysts is that they can be reused[3]. This is desired from both economic and environmental perspectives, as less catalyst is needed and less waste is created from the process.

Based on the mentioned improvements and investigations, a techno-economic assessment could be done to evaluate how the system would perform on an industrial level. The biphasic system has the advantage of eliminating an extraction step in the downstream processing, by including the octanol phase inside the reactor[8]. In conventional processes, ethyl acetate can be used to extract the aromatic monomers after the reaction[32]. On one hand, eliminating a downstream processing unit could cut down on operational and investment costs, but the usage of octanol could still make the process more expensive and complicate the product purification. For a lignin valorisation process to be economically and environmentally feasible, there are some factors that should be considered. Due to the large volumes of lignin produced globally, it is important that the process has the capacity to convert high volumes of lignin into value-added products. Further, costly stoichiometric reagents should be avoided and the solvent costs along with the decomposition and inhibition of catalysts and substrate should be considered.[19] The BPD system needs further investigation and development to better fulfil the criteria of converting larger amounts of lignin and not using an excess of catalyst.

The production of 5-nitrovanillin from lignin could also be investigated further. Different nitrate salts could be tested to evaluate how the cation affects the process, and nitric acid could be used as the aqueous phase in the BPD system. To investigate the formation of 5-nitrovanillin, tests could be done using vanillin as a model compound. This could give clues about reaction pathways when using lignin instead, but it should be noted that the use of model compounds is not always representative of how the system behaves when using real lignin[3, 48]. Lignin depolymerization with nitrate salts could potentially be a new and more sustainable route for production of 5-nitrovanillin, but market demands need to be investigated in order to determine how the process compares to conventional processes. It might also be feasible to produce 5-nitrovanillin from lignin-derived vanillin instead, which still would make the process free from fossil-based raw materials.

4 Conclusions

Different iron-, cobalt- and copper-based catalysts have been screened homogeneously and heterogeneously for biphasic oxidative depolymerization of Indulin AT. The best catalysts with regards to yields were iron(II) and iron(III) chloride when used homogeneously and the iron-containing heterogeneous catalysts. The maximum yield achieved was 1.1 wt-% of vanillin, for iron(II) chloride, which is an increase by 175% compared to when no catalyst was used. The yields were around 1 wt% for the best performing homogeneous and heterogeneous catalysts, which could be due to oxygen depletion in the system. Iron-based catalysts are generally the best performing catalysts for achieving high yields of vanillin in the BPD system and have a higher selectivity for vanillin. Copper-based catalysts on the other hand produce a more diverse product pool, with lower selectivity for vanillin. For the homogeneous catalyst screening, the chloride salts generally favoured vanillin production, although for copper-based catalysts the difference between the counter ions is not significant. When nitrate salts were used, nitrated aromatic monomers, such as 5-nitrovanillin, and aliphatic diacids were formed, which were not found in any other samples. The 5-nitrovanillin yields were under 1wt%, but if further investigated the BPD system could be a sustainable method for production of 5-nitrovanillin. The BPD process needs further development, and more testing could be done to evaluate the system and the feasibility of operating at industrial scales.

5 References

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Appendix A – Calibration curves

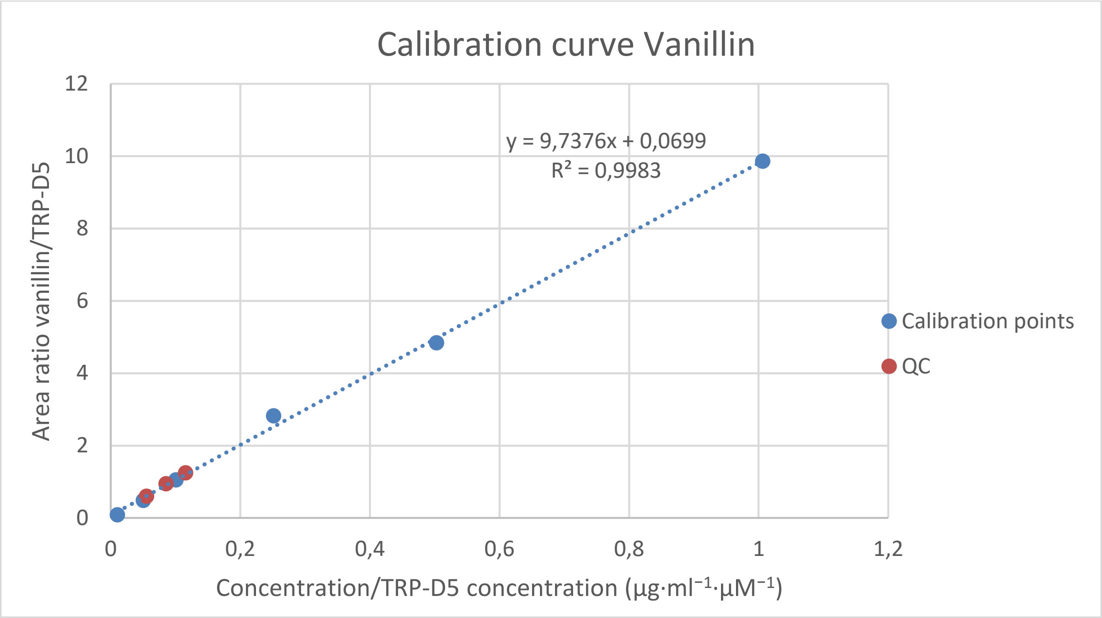

Figure A1: Calibration curve for Vanillin.

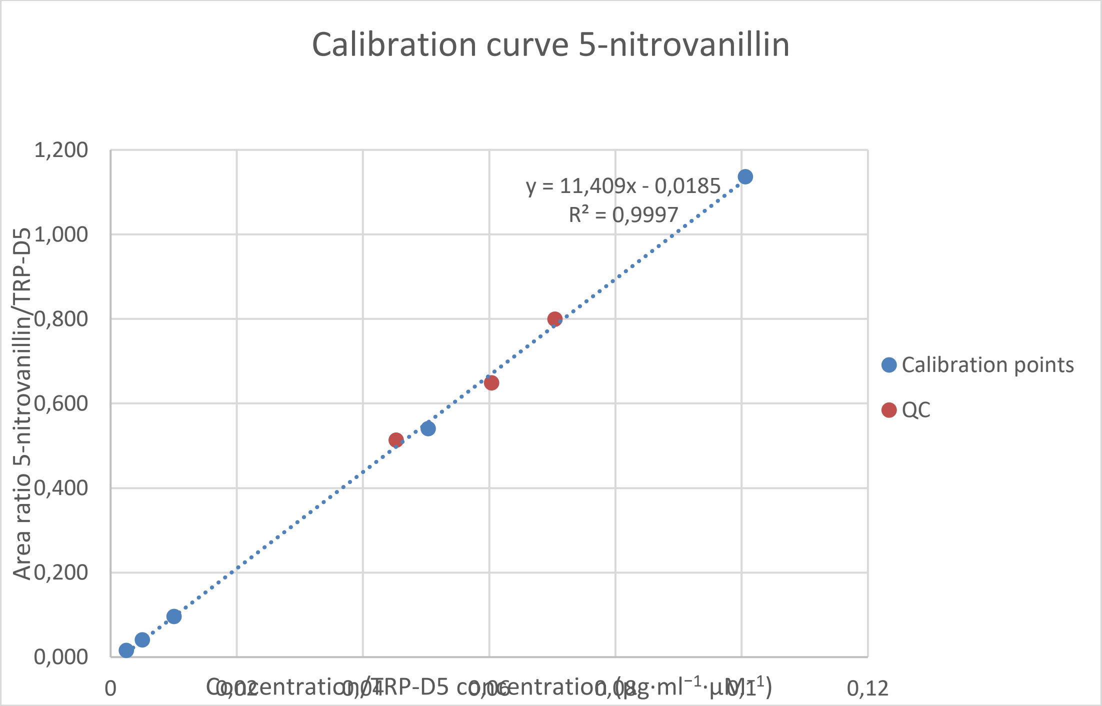

Figure A2: Calibration curve for 5-Nitrovanillin.

Appendix B – Hierarchical cluster analysis

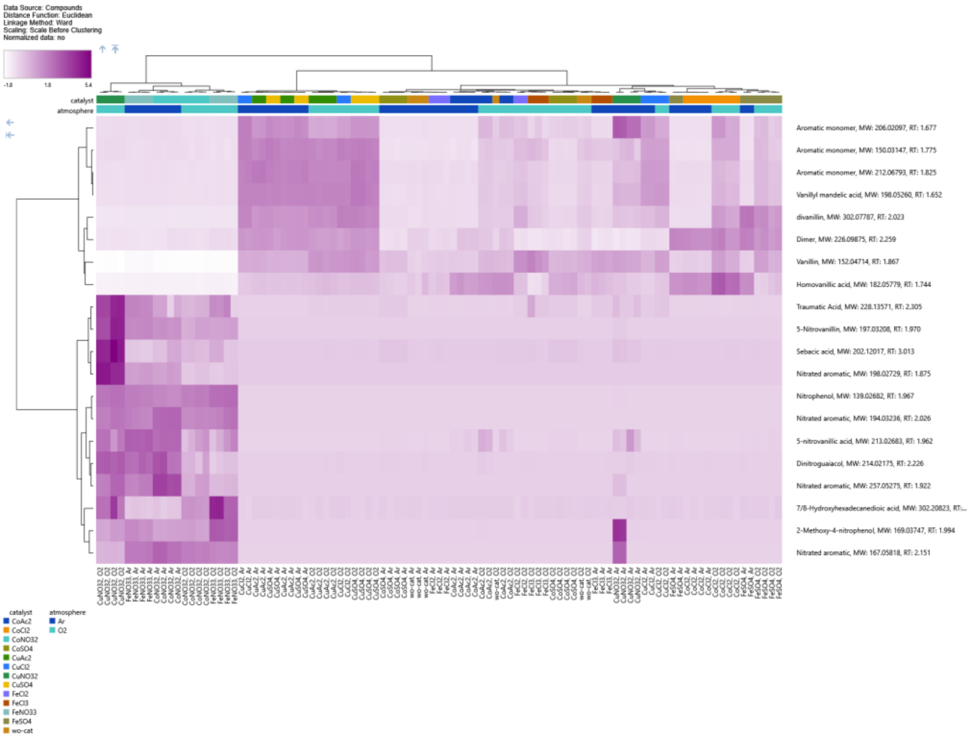

Figure B1: Hierarchical cluster analysis of data from homogeneous catalyst screening.

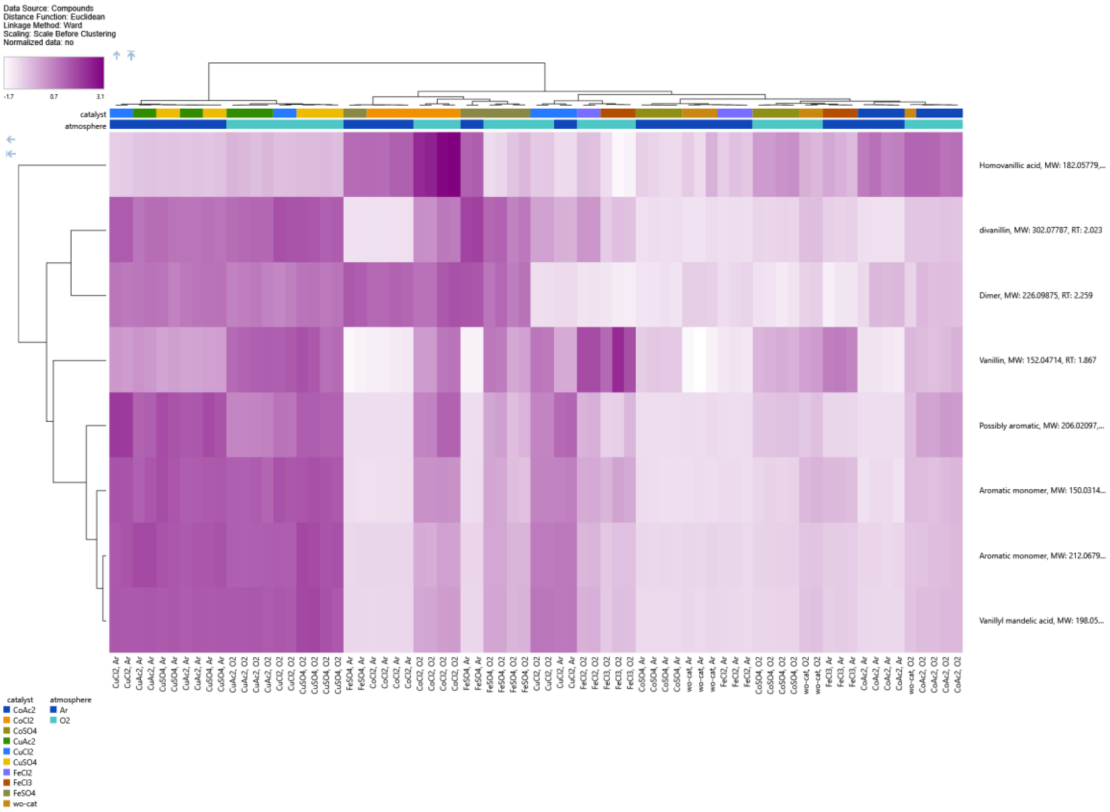

Figure B2: Hierarchical cluster analysis of homogeneous, non-nitrate catalysts.

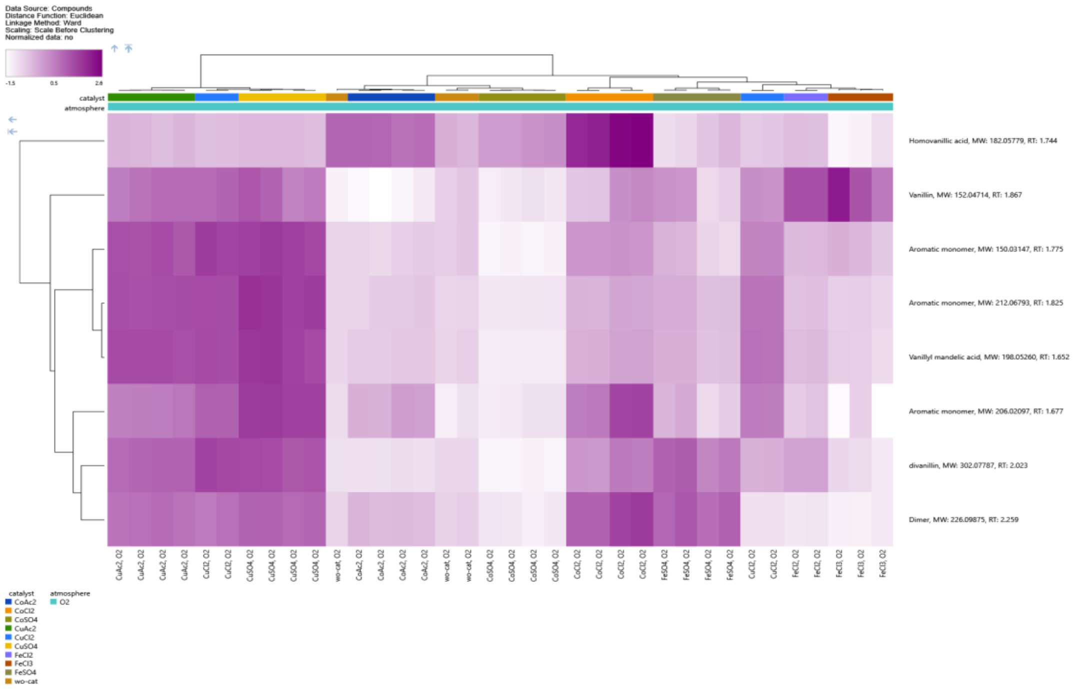

Figure 7: Hierarchical cluster analysis of homogeneous, non-nitrate catalysts in oxygen atmosphere.

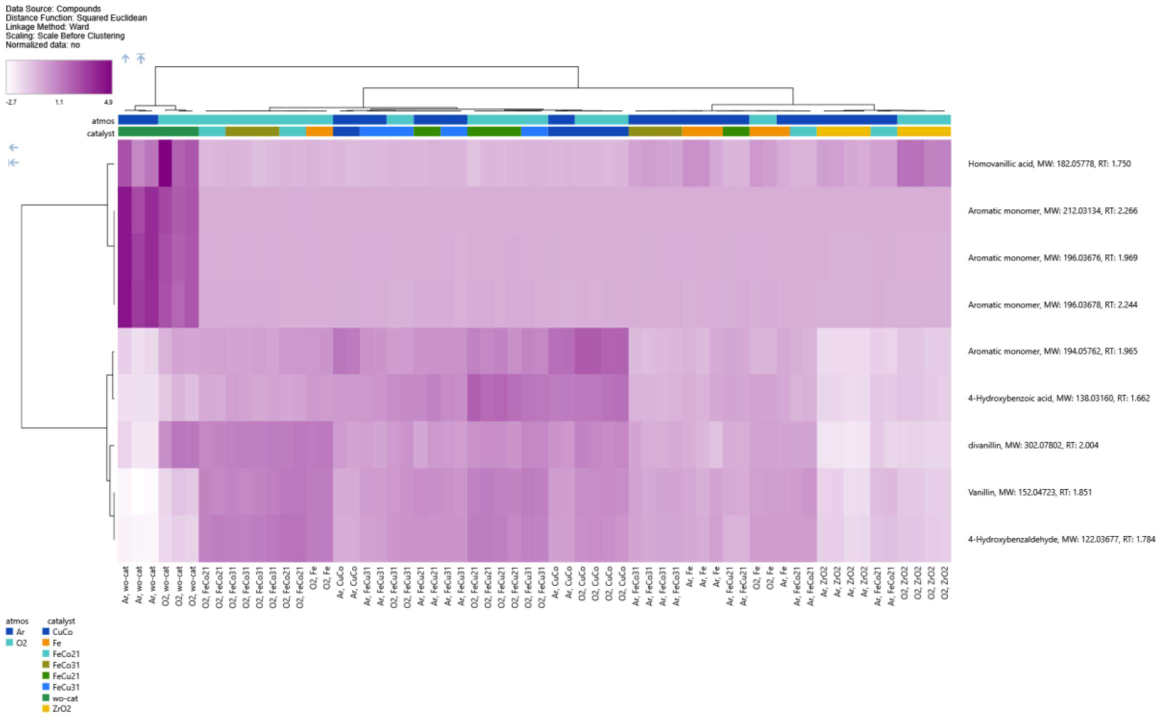

Figure B4: Hierarchical cluster analysis of heterogeneous catalysts.

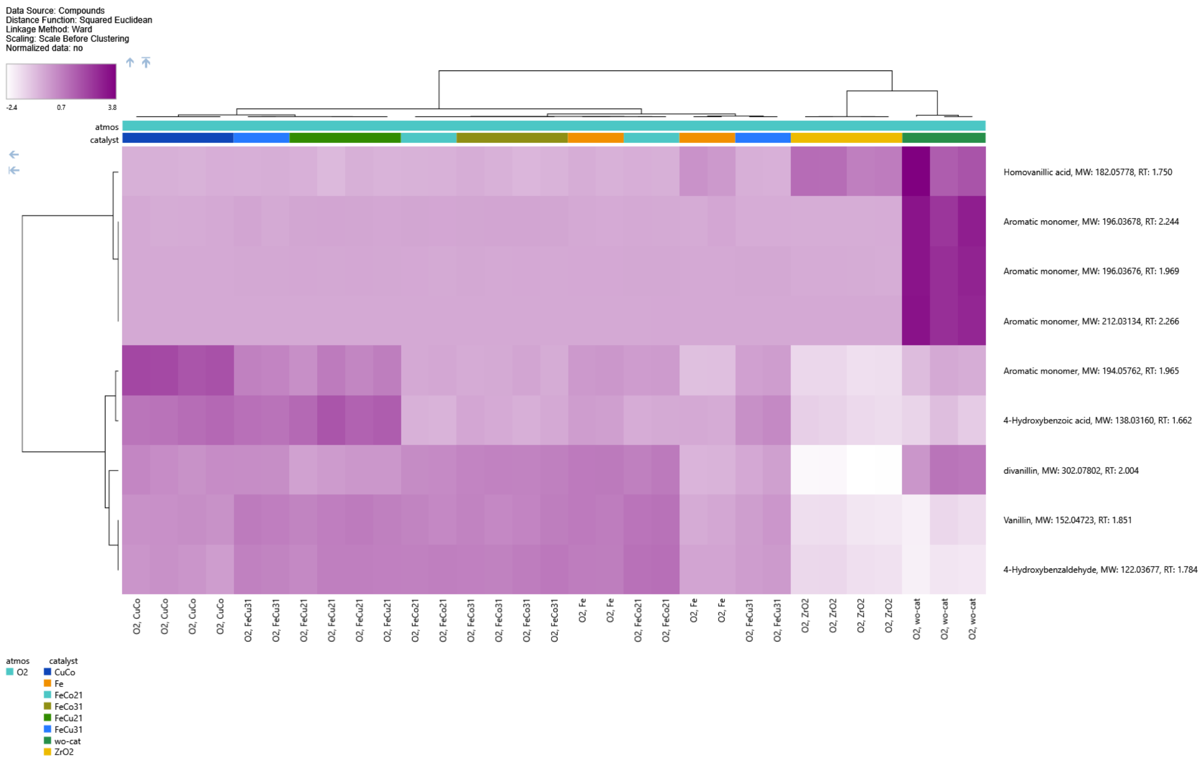

Figure B5: Hierarchical cluster analysis of heterogeneous catalysts in oxygen atmosphere.

Appendix C – XRD spectra

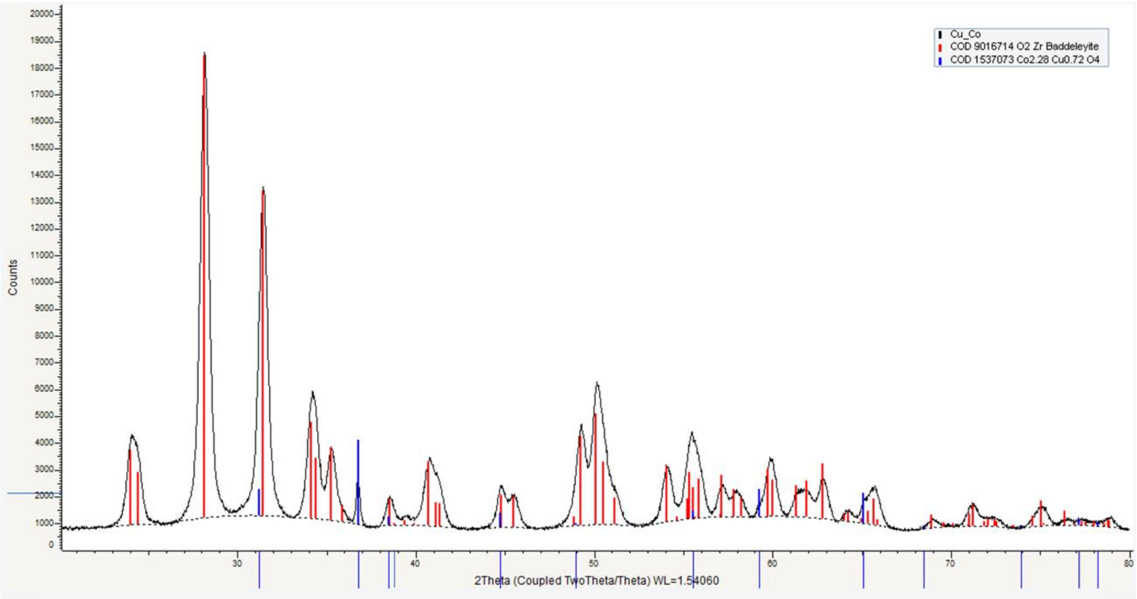

Figure C1: XRD spectra for CuCo catalyst.

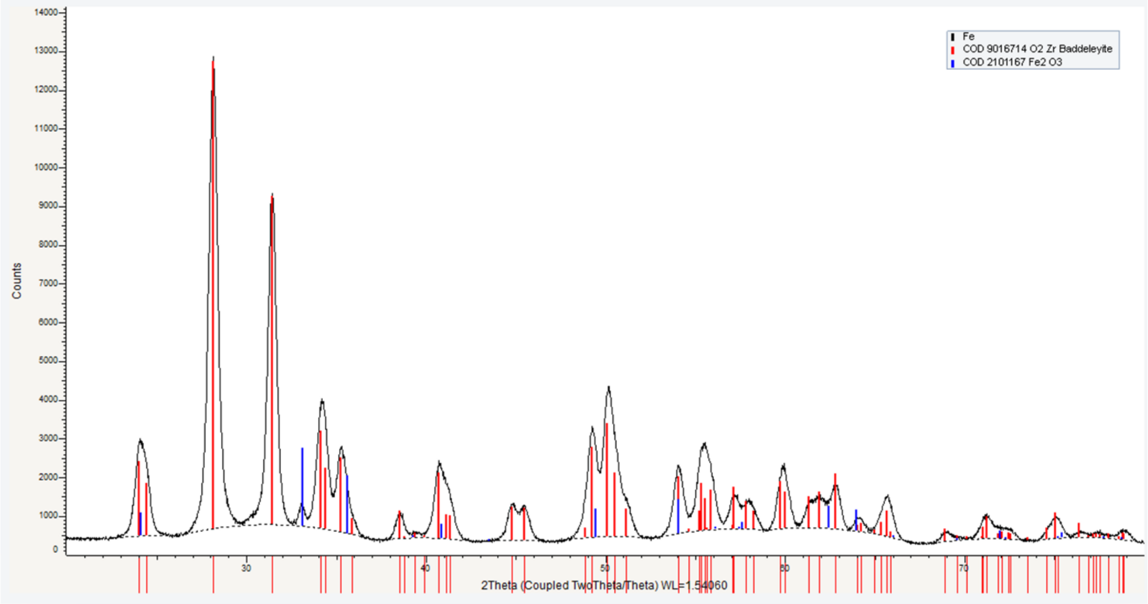

Figure C2: XRD spectra for Fe catalyst.

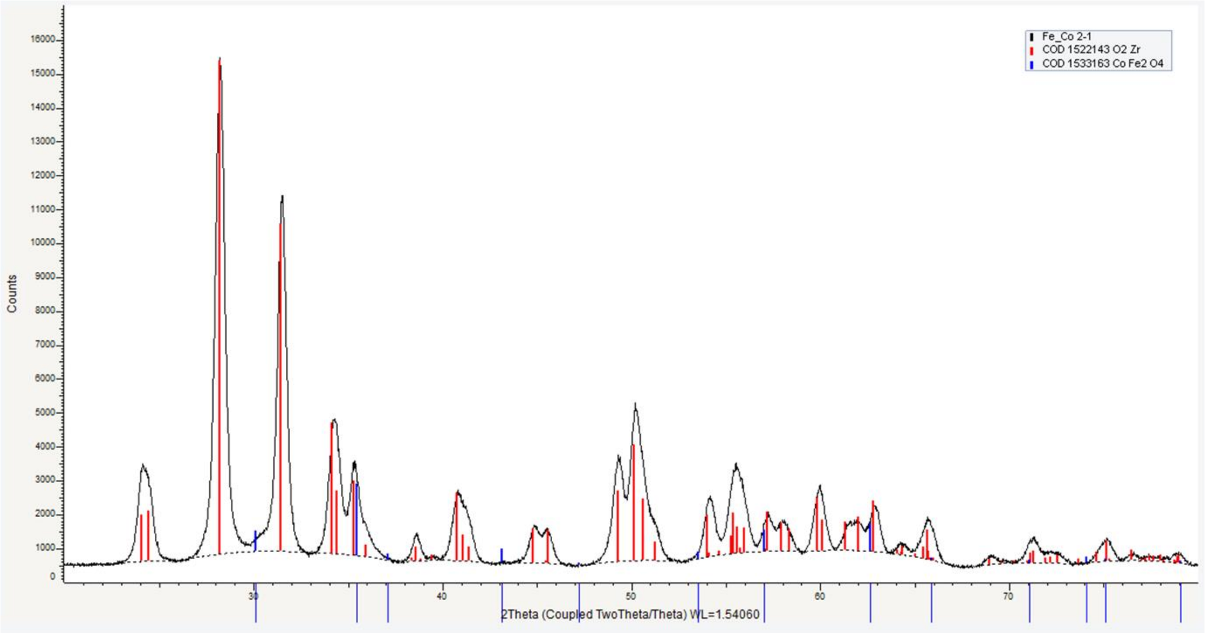

Figure C3: XRD spectra for 2:1 Fe:Co catalyst.

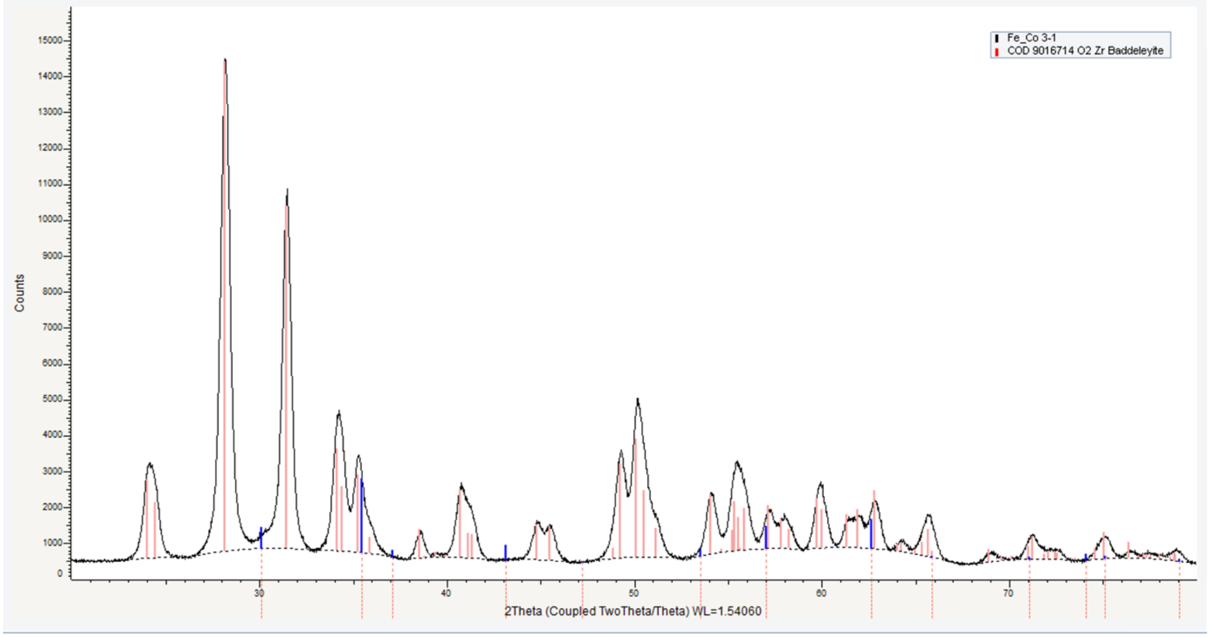

Figure C4: XRD spectra for 3:1 Fe:Co catalyst.

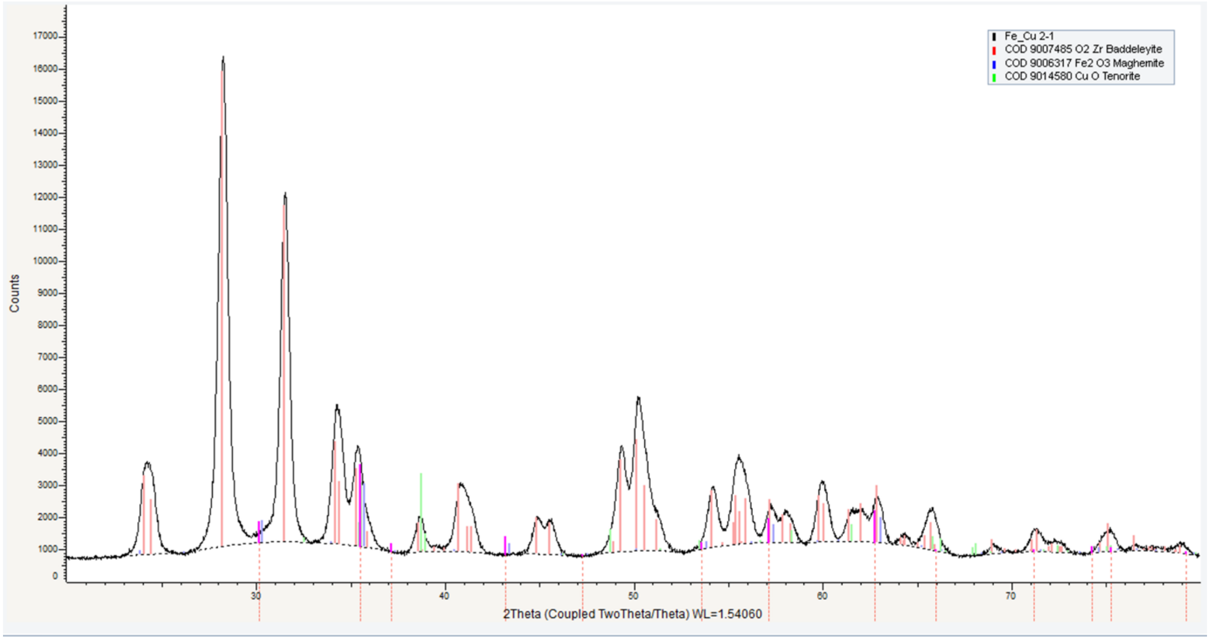

Figure C5: XRD spectra for 2:1 Fe:Cu catalyst.

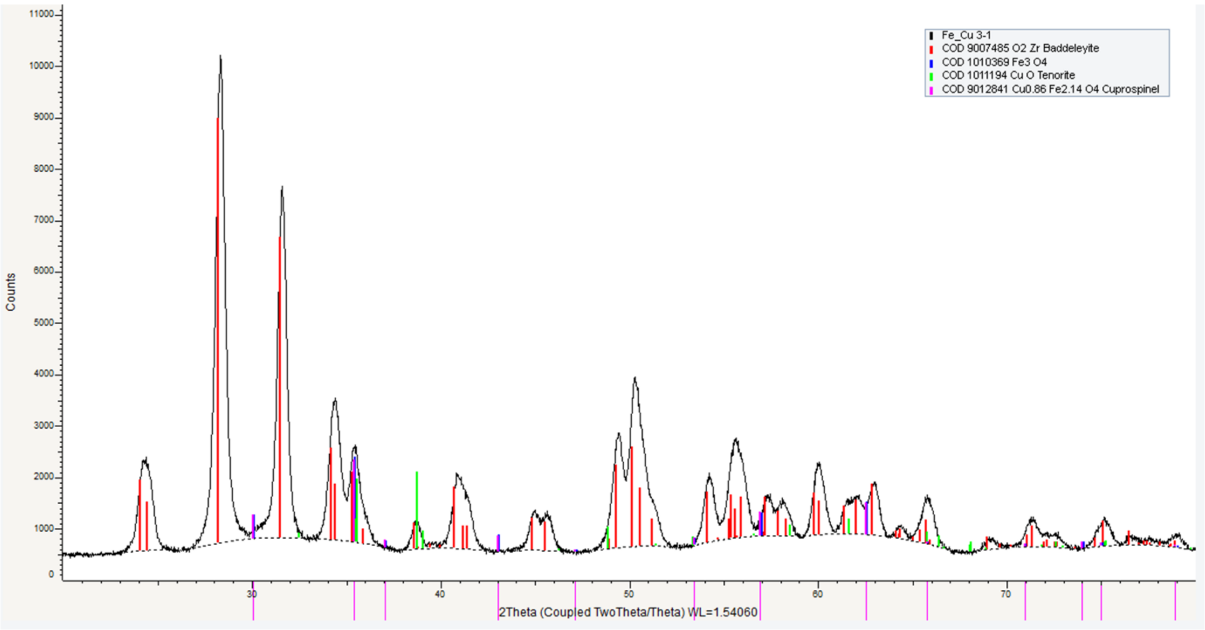

Figure C5: XRD spectra for 3:1 Fe:Cu catalyst.