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THE ROLE OF CATALYSIS IN THE VALORIZATION OF WOODY BIOMASS **FAST PYROLYSIS LIQUIDS**: Overview and contribution of IRCELYON.

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Abstract

The objective of this review article is to focus on the role of catalysis in the various pathways involved in the value chain of **fast pyrolysis liquids** produced from wood. During the last 15 years, IRCELYON has been involved in many of these routes. This article is mainly focused on the role of catalysts in bio-**liquid** conversion and co-processing with **petroleum** feedstocks. **We provide relevant references for each pathway and focus on the specific contributions of IRCELYON and on the most recent studies, not covered by previous reviews.**

Key Words: Fast pyrolysis, bio-**liquids**, catalysis, co-processing, reforming, upgrading

1. Introduction

Fast pyrolysis (FP) has been investigated since 1975 and has now reached industrial scale with the appearance of various technologies and large-scale units for producing **pyrolysis liquids** [1,2,3]. Whatever the type of reactor or biomass used during the FP process, post treatments are generally required to upgrade the complex matrix of oxygenated compounds obtained, **although fast pyrolysis liquids can be directly used as low-grade heating fuel.** The **major** interest of FP is the high **liquid** yield (up to 75%) that can be reached. However, crude bio-**liquids** have limited applications due to their acidity, high viscosity, thermal instability and high oxygen **and water** content [4,5]. **Further** complexity arises from the presence of macromolecules **such as "pyrolytic lignin"**. Therefore, upgrading is **usually** required and, for the last 30 years, investigations attempted to obtain fuels or chemicals **by cheap processes**, exploring different pathways. Thus, in 1983, Rolin et al. [6] investigated the impregnation of biomass with different salts and their impact on FP, Elliott et al., [7], in 1984, explored the hydrodeoxygenation (HDO) of FP **liquids** and **Diebold** et al., in 1988, the conversion of FP vapors [8]. The use of fluidized bed reactors suggested that the Fluid Catalytic Cracking (FCC) refining process can be transposed to pyrolysis **liquids** in so called BFCC (Bio **Fluid** Catalytic Cracking) or CFP (Catalytic Fast Pyrolysis) using acidic catalysts (essentially zeolites). HDO catalysts adapted to fluidized bed were also applied in Reactive Catalytic Fast Pyrolysis (RCFP) in the presence of hydrogen.

The composition of a FP bio-**liquid** corresponds to a mixture of numerous oxygenated compounds. The three most abundant components are acetic acid, 1-hydroxy-2-propanone

and levoglucosan, issued from cellulose. A wide family of phenols, guaiacols and syringols originate from lignin, as do many aldehydes, ketones, carboxylic acids and alcohols. This composition is illustrated in a GCxGC chromatogram (Figure 1). Only 30-40% of the bio-liquid components can be quantitatively analyzed by gas phase chromatographic techniques (GC-MS or GCxGC-FID).

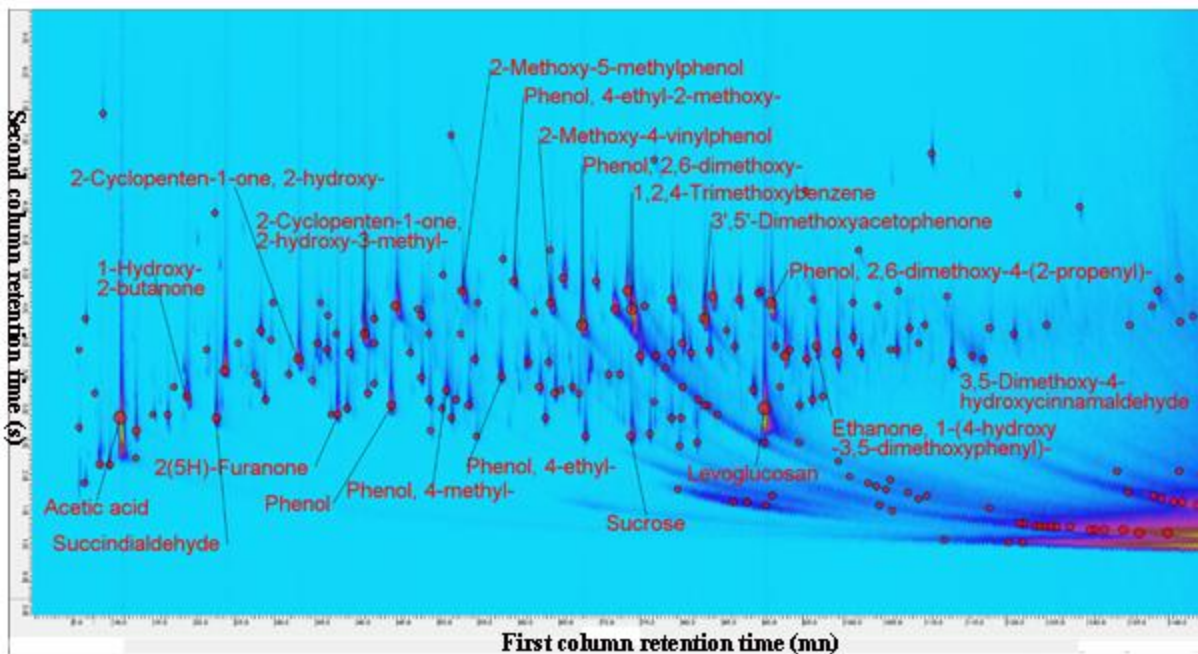


Figure 1. Comprehensive GCxGC analysis of fast pyrolysis liquid of forestry residue produced at 520 °C (residence time 1-2 sec) with Ensyn type technology by VTT (20 kg/day).

Many oligomers cannot be vaporized due to their high boiling points, above temperatures where polymerization and/or cracking reactions take place. They are therefore not detected by GC methods. Usually, a rough idea of the complexity of these oligomers is obtained by Size Exclusion Chromatography (SEC), but a more comprehensive analysis can be reached by a petroleum-inspired approach. This is achieved using ultrahigh resolution mass spectroscopies such as Fourier-transform ion cyclotron resonance FTICR-MS [9,10,11,12] or OrbitrapMS [13,14]. Ionization modes and dopants used for this purpose strongly influence the detected species. Nevertheless, it gives a clear insight in the complexity of these heavy compounds, with several hundred compounds detected and considered as oligomers, pyrolytic lignin or humins, as illustrated in Figure 2. It is obvious that such a complexity is not suitable for transportation fuels and it requires a further upgrading or a modification of the pyrolysis process. The heavy compounds observed are typically in the range of C₁₀-C₃₀ and contain several oxygen atoms (from 2 to 15 but mainly 4) and exhibit DBE's (double bond equivalent) values from 5 to 20, indicative of aromatic entities.

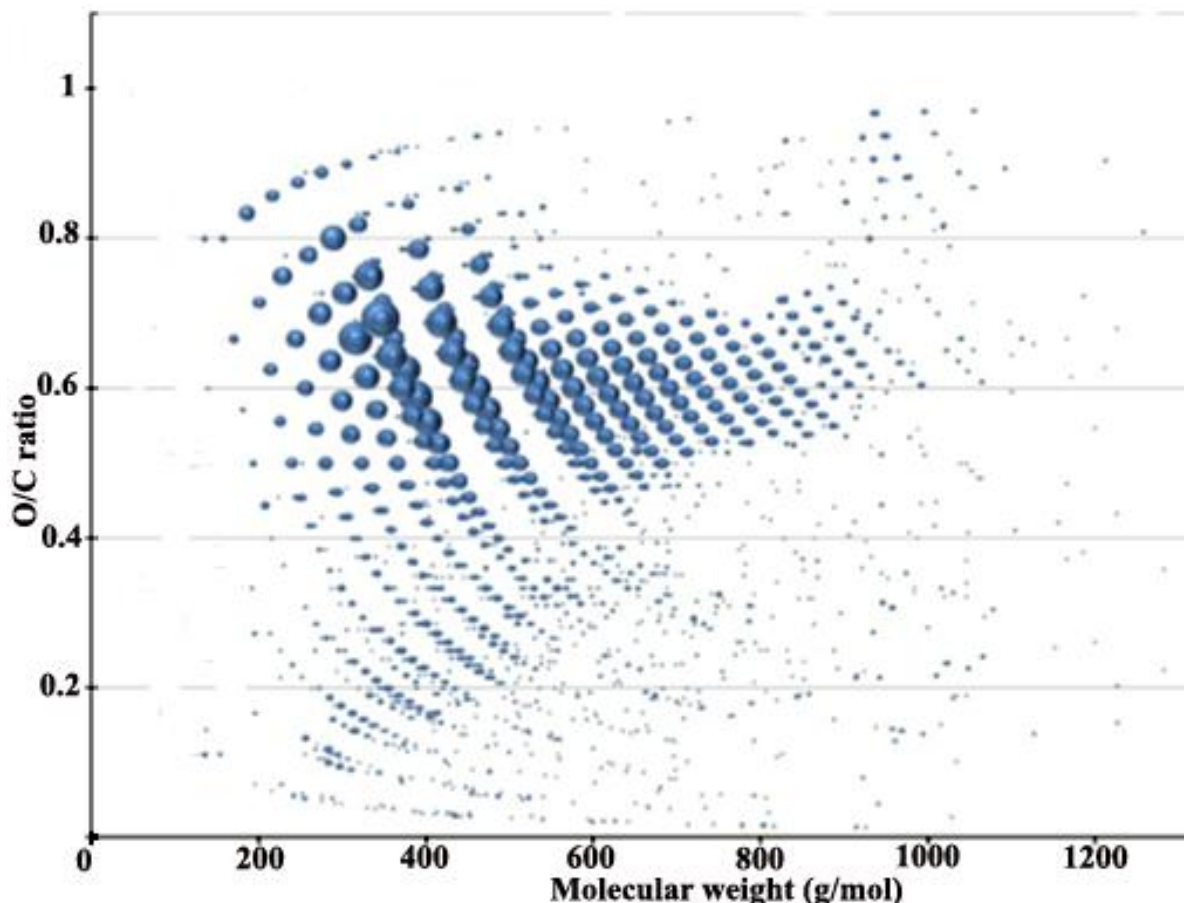


Figure 2. O/C ratio as a function of molecular weight for the data obtained by ESI(+)-FT-ICR/MS analysis of “syrup” fraction of a fast pyrolysis liquid of beech wood produced at 500°C in a fluidized bed reactor, adapted from ref [12].

Therefore, many studies attempted to upgrade these FP liquids into more valuable products, such as cuts for transportation fuels or aromatics, and in most of them catalysts were used to reduce the oxygen content as much as possible. Upgrading technologies can either use physical methods, such as solvent addition, filtration or emulsification, or chemical upgrading. This review will focus on the latter approach. In fact, a competitive value chain for FP liquid technology requires a combination of processes where catalysis has a determinant role on products quality and cost reduction. There are many ways to introduce catalytic steps, which can be summarized by Figure 3, together with the targeted products. Catalysts can be involved either at the earlier stage of FP, as catalysts impregnated on the biomass, or directly in the pyrolysis reactor, or downstream by catalytic treatment of the pyrolysis vapors, or by ex-situ upgrading of pyrolysis liquids.

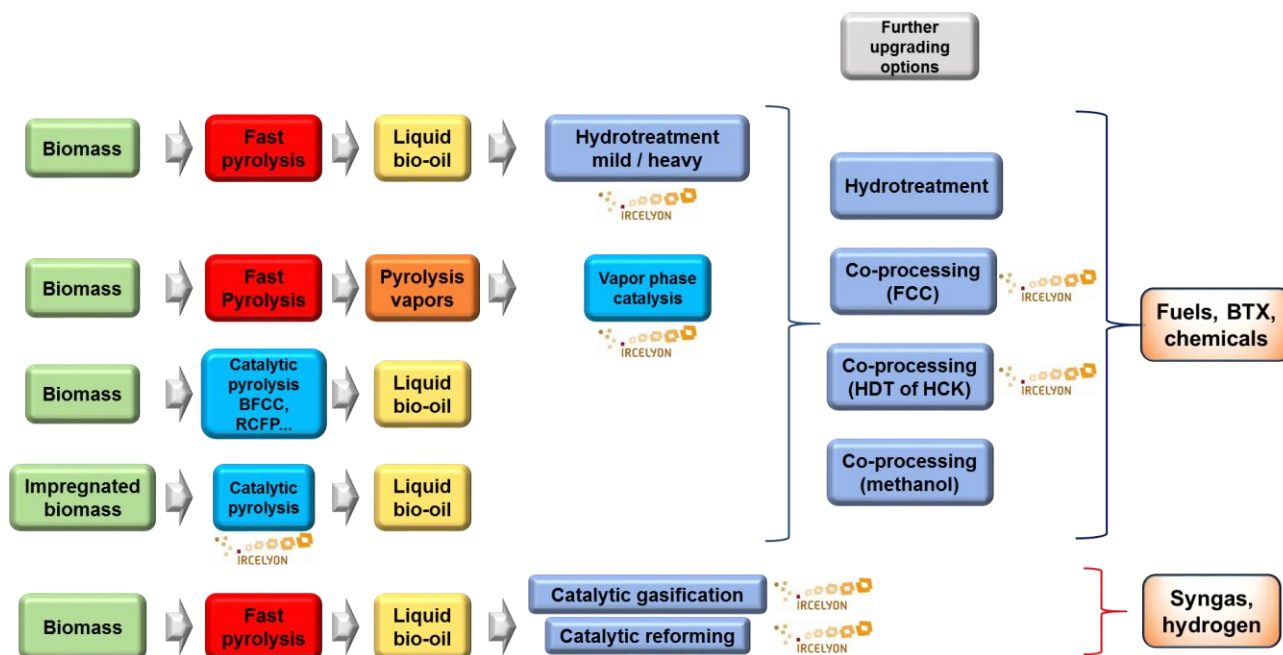


Figure 3. The various options of fast pyrolysis/catalysis pathways for fuels, chemicals or hydrogen production. (Catalysis involved in blue boxes).

Whatever the pathway used, a final conversion process is often required (either hydroconversion or cracking) in order to fulfill the quality requirements of transportation fuels. IRCELYON has been involved in many of these topics as depicted by Figure 3 and its contribution will be detailed. All these aspects will be exemplified hereafter with the intent to underline the chemical impact of the catalysts on the product distribution and on reaction pathways.

Figure 4 illustrates the impact of different catalytic conversion methods (studies from IRCELYON and detailed below) on the composition of the bio-liquid.

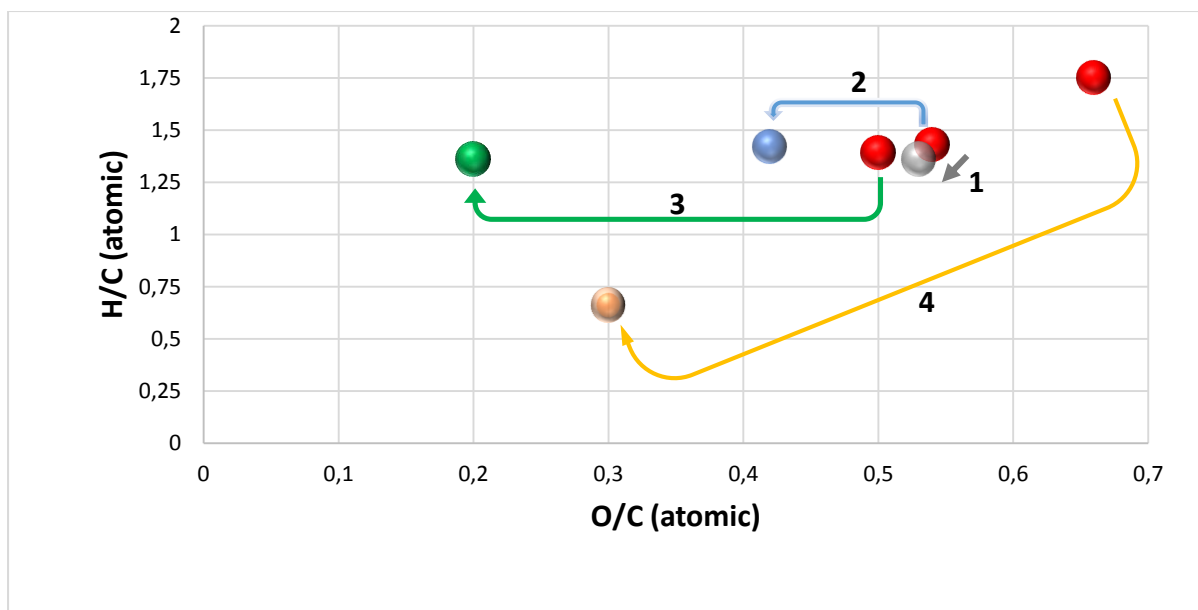


Figure 4. Illustration of the impact of conversion process on bio-liquid composition: starting composition (●), impregnated CeO₂ (1), vapor cracking with CeO₂ supported on char (2), hydrotreatment with NiMo/Al₂O₃ reduced catalyst (3), and HMFI zeolite (4).

2. Catalysis during the pyrolysis process

2.1. Biomass impregnated by catalyst precursors

The community of fast pyrolysis questioned early on, the role of ashes in the fast pyrolysis process and the capability of these solids to catalyze the biomass conversion. In fact, biomass contains inorganic compounds such as alkali, alkaline earth metals, silicon, phosphorous and transition metals (Mn, Zn, Fe,...). Si (as SiO₂) and K are the main inorganics (SiO₂ 2-100 ppm, K₂O 2-50 ppm) [15]. In the early studies on pyrolysis, the presence of K compounds was found to enhance the reactivity of char [16]. The primary mechanism of the biomass conversion is usually divided into three pathways: char formation, depolymerization and fragmentation. Secondary mechanisms such as cracking and recombination, which increase the complexity of molecules formed, are also occurring [17]. In all cases, catalytic sites might be involved in all processes, but considering the short residence time of the FP, thermal contribution and radical chemistry have a dominant role in the reaction and product formation. Nevertheless, many reactions such as decarbonylation, decarboxylation, dehydration, ketonisation, esterification, heterolytic scissions.... can occur and be catalyzed even if the contact time of the process is short.

Therefore, many attempts to add or impregnate mineral compounds on the biomass were done. The studies involved lignocellulosic biomass as well as its individual components (lignin, cellulose, and hemicellulose). The different mechanisms of fast pyrolysis such as

depolymerisation, fragmentation and undesired carbonization, can be affected by the presence of these catalysts. A long list and references of soluble minerals used in FP by impregnation of the biomass was recently given by Shaifzadeh et al. [18], therefore we provide here only additional references. The impregnated compounds can be classified into three families, described below. Note that the nature of the anion salt can play a significant role, since, for instance, nitrates can form nitric acid and acetates acetic acid during the pyrolysis. The nature of the reactor also affects residence time or heat exchange (fixed bed versus fluidized bed, TGA, Py-MS) and influences the role of the impregnated phase. Activation methods, for instance micro-wave exposure which can interact with salts or with oxides (interaction which can be size dependent) can induce specific effects such as thermal runaway. The use of individual components of the lignocellulose also helped to discriminate the specific roles of impregnated compounds. Often cellulose, hemicellulose or lignin were treated independently in order to clarify the reactivity of the 3 constituents of the lignocellulose. Considering a process aspect, the low cost of catalysts is mandatory according to the loading used (generally in the range of a 1-5 wt.%), and impregnation strategies can hardly be commercialized. The studies on impregnated phases are generally lacking characterization of the catalytic functions after reaction.

Role of alkali or alkaline earth salts

Many studies have been dedicated to the impregnation of Na, K, Mg or Ca salts (mostly carbonates, chlorides, acetates) and their impact on pyrolysis mechanisms and their implication in acid base properties. These compounds usually favor the formation of solids and gases and modify the composition of the bio-liquid. Besides thermal effects (usually a decrease in the activation temperature, particularly with alkaline earths), they can affect the primary mechanisms. For instance, the use of KOH (from 0.2 to 0.6 wt.%) decreases the formation of anhydrosugars and favors phenol formation. Above 1 wt.%, these effects disappear [19]. Some effects can be attributed to the reactivity of the individual components of ligno-cellulosic biomass: this is illustrated in Figure 5 identifying the role of catalysts on cellulose conversion and products formation in the absence or presence of alkali.

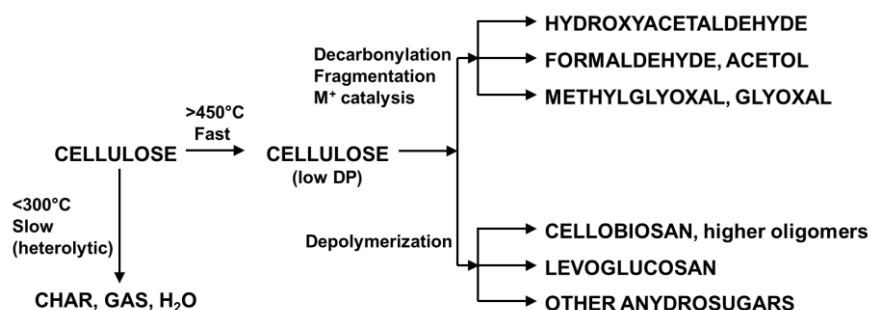


Figure 5. Mechanism of thermal decomposition of cellulose by fast pyrolysis in the presence and absence of alkaline cations adapted from [20].

More specifically, Na, K and Ca chlorides reduce levoglucosan production and **modify the distribution of low molecular weight products (for instance increase of furfural, decrease of levoglucosan)**, even at low level of addition (0.005 mole of chloride/mole of glucose unit) [21]. Thus, in the case of cellulose, the depolymerisation route leading to levoglucosan is altered **by alkali** (or alkali earth) towards the fragmentation route to produce 1-hydroxy-2-propanone, 1-hydroxy-butanone and acetic acid. Concerning the lignin conversion, [22], Mg and Ca hydroxides were found to modify the char structure, enhance CO₂ emissions and increase phenols formation. Note that MgO or Ca salts lead to lignin agglomeration, behavior attributed to too strong basic properties. During straw pyrolysis, species such as Cl⁻ can be volatilized at rather low temperature (200-400°C) [23].

Role of transition metal salts

Similarly to alkali metals, transition metals affect both **primary and secondary mechanisms** of FP. The recent and comprehensive review of Sharifzadeh et al. [18] has compiled different Cu, Fe, Mg and Zn salts and underlined the increase of lighter molecules produced; other references are added below. The use of **transition metal salts** broadens the variety of catalytic functions, either acid base or redox. If the metal is reduced during the process by carbothermal reduction (i.e. Ni, as demonstrated by XPS in [24]), hydrogenating or hydrogenolytic functions are obtained. As previously observed with alkali, carbonization and depolymerisation pathways are modified, but the nature of the metal reveals more important effects. For instance, the presence of Ni decreases the **liquid** yield and reduces benzene and polyaromatic hydrocarbons (PAH) concentrations. It also increases the gas yield and more specifically H₂ production. Fe reduces the production of organic fraction and of light hydrocarbons [25]. Using a series of metal nitrates (Ce, Mn, Fe, Co, Ni, Cu, Zn) impregnated on Eucalyptus **biomass**, either at atmospheric pressure or under vacuum (which promotes the metal insertion **into** the biomass), Eibner et al. [26], using a tubular fixed bed reactor, observed that anhydrosugar yields (3,6-dioxabicyclo[3.2.1]octan-2-one (LAC) and levoglucosan) were deeply affected by the presence of catalysts such as Zn, Co (**nearly 20 times increase in LAC yield**), whereas Ni, Mn and Ce **promoted** CO₂ formation. On the contrary, Zn and Co seem to favor cellulose depolymerisation whereas iron inhibits it. Mg induces recombination of levoglucosan and small molecules to form large compounds such as oligomers and chars [27]. The role of counter anions of Cu and Fe salts was shown by Richards et al. [28], who evidenced the role of Brønsted acidity in levoglucosenone formation. Under FP conditions, transition metals are recovered on the coke and well dispersed on its surface. These metal doped chars can be used as catalysts for FP vapor conversion (see section 2.3).

Role of organic acids or ammonium salts

Organic acids were considered for improving the depolymerization of cellulose by fast pyrolysis in order to obtain high yields of **levoglucosan and levoglucosenone**. Early studies were performed, for instance, in the late seventies by Shafizadeh et al. [29] who investigated the benefit of impregnation with phosphoric acid, selected for its low volatility,

and optimized its content for getting high yields of sugar derivatives . This topic of cellulose pyrolysis was revisited more recently by Dobele et al. [30, 31] and also applied to birch wood, leading to the same conclusion on the beneficial role of acids in transglycolation and dehydration reactions. Acids can contribute to the degradation of the cellulose by acid hydrolysis before the pyrolysis. Impregnation of orthophosphoric acid or ammonium phosphate led to the same conclusions with furfural and levoglucosenone becoming dominant compounds and more char produced [32].

To conclude, impregnation of mineral salts or organic acids have impacts on the gas, liquid and char yields, which can drastically differ depending on the nature of the cation, but also the counter anion employed. The impact on the oxygen content in the bio-liquid is weak and recycling the impregnated elements on the raw biomass, usually deposited on chars after pyrolysis, must be emphasized.

2.2. Biomass fluid catalytic cracking (BFCC) and reactive catalytic fast pyrolysis (RCFP)

BFCC is the transposition of the oil refining FCC process to FP. It means that the conventional fluidized bed medium (sand, ...) is replaced by a catalyst, which in principle needs to be periodically regenerated. Catalysts can also be added to other reactor types than fluidized beds. Depending on the catalyst nature and if whether or not the catalysts regeneration is required, the process is run with an inert gas (BFCC) or with a mixture containing hydrogen (RCFP), possibly under H₂ pressure (Gas Technology Institute (GTI) technology). As a transposition of FCC, zeolite-type catalysts such as ZSM-5, mordenite, faujasite, ferrierite and Beta zeolites were investigated in depth [1]. These zeolites can also be modified by introduction in the framework of alkali, alkali earth, transition metals or even noble metals. In the case of RCFP, strong acidity is not necessarily required and HDO catalysts can be preferred, as illustrated by Wang et al. who compared the performances of solid acid (silica alumina), metal oxide (iron based or Mo based) or sulfide catalysts [33]. Molybdenum-based reducible metal oxide catalysts and commercial hydrotreatment (HDT) provide the best deoxygenation performances. Depending on the catalyst, the O content in the product can be below 10 wt.%.

Early studies investigated the catalytic cracking of pyrolytic liquids, but an ideal process would convert directly the raw biomass in this FCC like process. As compared to other routes, this process has achieved industrial scale development through the KiOR process [34], with a plant opened in 2011. However, the company faced many production issues and declared bankruptcy in 2014. A critical review of catalytic pyrolysis was given by R. H. Venderbosch [35] evidencing the lack of efficient catalysts to obtain products of interest with a sufficient yield. This type of approach was reconsidered recently by Anellotech (in a joint venture with IFPEN, Johnson Matthey, Axens). They commercialized the Bio-Tcat™ Process, dedicated to BTX and C₉₊ aromatics production, using ZSM type zeolites [36]. The process was operated for 4000 hours on stream and targeted BTX production. Similarly, Research Triangle Institute (RTI) developed an integrated process based on catalysts

containing metal oxides on zirconia [37]. An alternative is also given by GTI with a process called IH². A fluidized bed reactor performing hydrolysis is used under high hydrogen pressures (10-17 MPa) with specialty catalysts supplied by CRI, and a consecutive hydroconversion process leading to bio-fuels [38]. Demonstration of the process was achieved in a pilot plant of 50 kg/day capacity and tested continuously over 750 h, producing gasoline and diesel fuels [39]. One of the key issues of these technologies is char separation, which seems to be overcome by controlling the size of the catalyst particles. Another issue is the deposition of alkali metals on catalysts, which can be solved by the pretreatment of biomass, for instance as done in the MinFreeTM process proposed by Anelotech. These three emerging technologies were described in detail by Perkins et al. [3].

2.3. Catalysis treatment of pyrolysis vapors

Compared to BFCC, the catalytic conversion of catalytic pyrolysis vapors has many advantages. Close-coupled vapor upgrading can take benefit of the heat of the pyrolysis process, the temperature of catalytic reactor can be controlled and hydrogen is not needed. The introduction of hot gas filtration can provide a beneficial control of the molecular distribution of vapors [40] and prevents the interactions of chars with the catalysts. Thus, using a fluid bed reactor (1 kg/h), Ruiz et al. observed that high temperature hot gas filtration promoted dehydration and decarboxylation by char cake formed on the filter.

Catalyst regeneration can be envisaged either in sequential or riser mode. A. V. Bridgwater [1] reviewed this approach until 2012 and underlined the need of more developments to validate the feasibility of this pathway. Most of the catalysts investigated at that time were zeolites (ZSM-5, FCC catalysts) or mesoporous (alumino)silicates (MCM-41, SBA-15), see for instance ref [41]. Zeolite catalysts induce many reactions and lead to the formation of aromatics. Later on, H-Faujasites with various contents of Na were further studied [42]. It showed that introduction of basic sites can be beneficial by controlling the acidity, reducing coke formation and modifying products distribution with less carbonyl and acidic compounds, but increasing phenols and hydrocarbons.

At IRCELYON we designed a reactor for catalytic treatment of pyrolysis vapors, which can provide accurate mass balances, online analysis of produced gases and allows recovering the catalysts for post-reaction characterizations [43]. One of the most striking observations is that after catalytic conversion of the vapors and condensation in a trap at 4°C, the bio-liquid directly separates into organic and aqueous phases. The use of acidic catalysts such as H-MFI or Ni supported on H-MFI led to the general trend observed in catalytic vapor conversion, i.e. lower bio-liquids yields and larger gas production. However, the quality of the bio-liquid is significantly improved with a larger fraction of monomers and a partial deoxygenation, as illustrated in Figure 6.

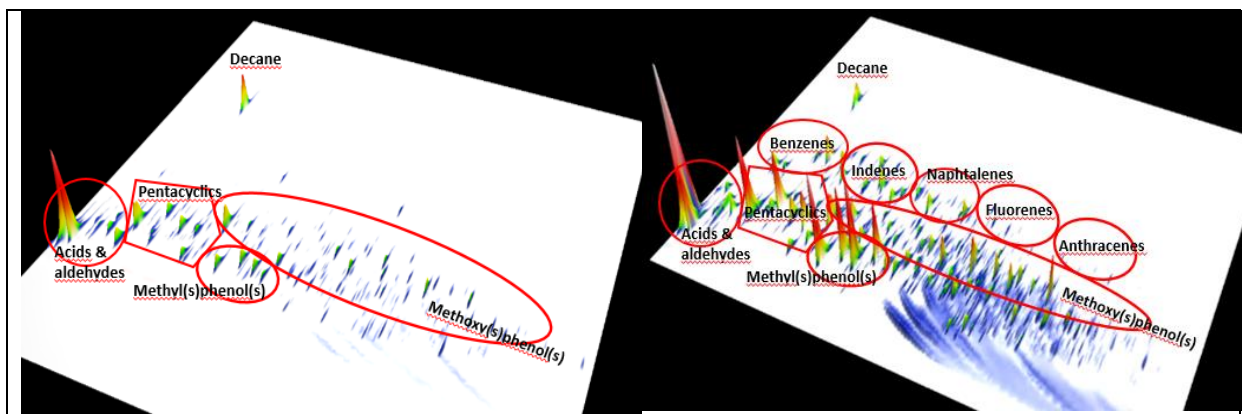


Figure 6. Comprehensive GCxGC analysis of pyrolytic liquid without (left) and with catalytic vapor conversion on HMF catalyst adapted from [44].

Regeneration of the catalysts by burning the coke deposits allowed a complete recovery of initial performances. The coke was burnt by TPO from 25 to 750°C (5°C/min, 10% O₂ in N₂), then the catalyst was tested again after regeneration.

A new trend in the field of catalytic conversion of vapors is the use of non-zeolitic or mesoporous catalysts. Instead of cracking reactions induced by a strong acidity, C-O cleavage (for instance by ketonic decarboxylation, or aldol condensation) and C-C coupling with simultaneous O removal are targeted using metal oxide catalysts. Typically, acetic acid, acetol, and the levoglucosan production is significantly reduced after the introduction of catalysts such as metal oxides or supported metals. Thus, various oxides such as TiO₂, ZrO₂-TiO₂ mixed oxides, alumina, ZrO₂, and MgO [45], various natural MgO or olivine [46], CeO₂ containing char [47] or Na₂CO₃ on alumina, [48] were investigated. In general, the oxygen content of the bio-liquid decreased, but remained in the range of 25-30 wt.%. Supported catalysts such as Ni₂P/SiO₂ or Pd/C [49], Ru/TiO₂ [50] were also tested in the presence of hydrogen in the feed (catalytic hydroconversion of FP vapors). After catalytic conversion, the bio-liquid becomes soluble in aromatic solvents such as tetralin, suggesting that subsequent co-processing with oil refinery feeds is technically feasible. These HDO-type catalysts can reduce more efficiently the oxygen content down to 10-20 wt.%.

To conclude, catalytic vapor conversion can drastically modify the product distribution and allows reaching a broad extent of deoxygenation. It provides the separation of organic and aqueous phases, reduces the bio-liquid acidity, converts many sugars and cleaves oligomers. More gases are also produced and the bio-liquid yield is reduced, but the products quality is drastically improved as compared to impregnated pyrolysis. After a first generation of acidic catalysts, oxides and metal supported oxides have been investigated and demonstrate good performances. Aspects of catalyst life time, optimization of cat/bio-liquid ratio and recycling in pilot scale units seems now necessary to consolidate this type of approach. However, it appears a good option to reduce, in a first stage and at moderate cost, the oxygen content and to improve oil quality.

3. Upgrading of pyrolysis liquids

Catalytic upgrading of FP liquids can be achieved by two different catalytic pathways: cracking or hydroconversion. The former attempts to break large molecules into smaller ones and to remove oxygen groups; the second pathway can proceed similarly with hydrocracking or in a milder way by hydrotreatment, which tends to prevent extensive C-C bond breaking and targets C-O hydrogenolysis. Mortensen et al. compiled a long list of different catalysts (metal, sulfides, carbides nitrides, acidic oxides, ...) implied in both routes [51], but most studies were conducted with model molecules. Another updated list can be found in the recent review of Sharifzadeh et al. [18]. The historical developments of this upgrading route were reviewed by Elliott [52] and later on by Bridgwater [1]. These studies used, at first, conventional CoMo or NiMo hydrotreatment catalysts, noble metal (Pt) or Ni catalysts, and later on Ru, Pd or zeolites. These early studies demonstrated that upgrading usually requires two stages: the first one is expected to provide at least a stabilization of the bio-liquid to prevent the formation of macromolecules and to reduce its acidity, whereas the second leads to high quality products by either deep hydrotreatment or hydrocracking. Typical operating conditions of this first stage, so called "mild hydrotreating", are a temperature range of 200-300°C, pressure range of 20-100 bar and WHSV range 5-10 h⁻¹. A third FCC stage was even proposed [53]. In terms of hydrogen consumption and extent of deoxygenation, Figure 7 illustrates each type of process (stabilization, mild HDO, second stage HDO) where experimental conditions allowed controlling the extent of deoxygenation. Hydrogen cost is the challenging economical aspect for this sequential upgrading pathway [53]. Alternative routes, using for instance physical methods (filtration, addition of surfactants) or chemical reactions (esterification, aldol condensation) [54], or cracking in supercritical ethanol were also proposed, but they never reached pilot scale [55].

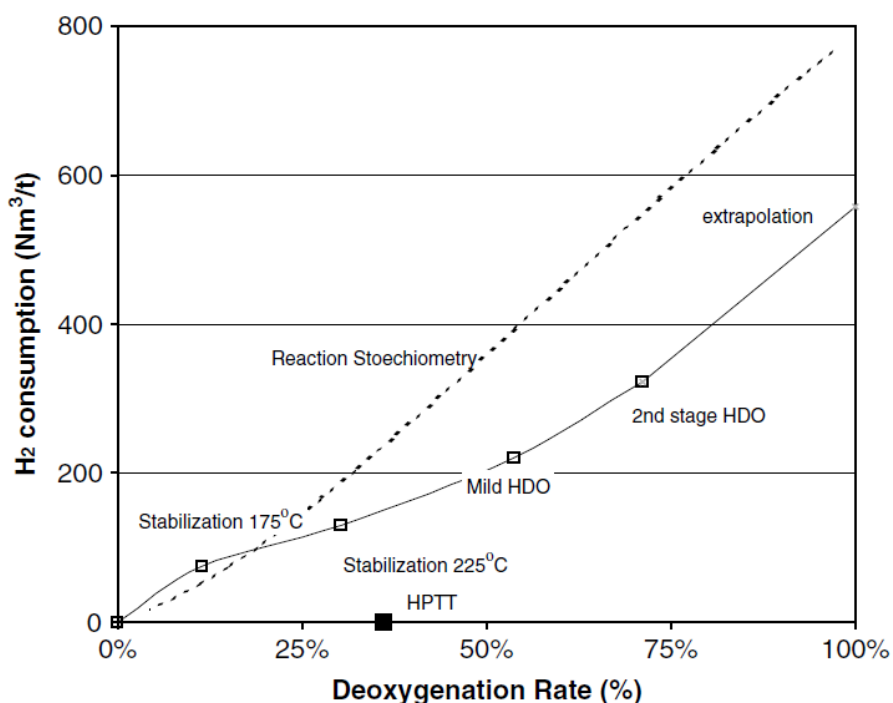


Figure 7. Hydrogen consumption versus the degree of deoxygenation (defined as $(1 - (\text{oxygen in product})/(\text{oxygen in bio-liquid}))$). From [56].

3.1. First stage upgrading and second stage hydrotreatments

Most of the studies performed with model compounds do not consider the specific reacting media of the bio-liquid. Hydrogen is used as reactant, but the presence of a large amount of water and of acetic acid implies some specificity of the catalyst, in order to resist to leaching or support degradation. Thus, a model bio-liquid was upgraded, in a 300 ml autoclave, by Fisk et al. with Pt supported on various oxides [57]. The presence of highly alkylated products was attributed to the acidic nature of the reaction medium. These specific conditions and their role on the upgrading were underlined by Wildschut et al. [58]. The competition between catalytic reactions and thermal reactions resembling those observed under hydrothermal conditions and leading to oligomers is of primary importance [35, 59]. Therefore, we will focus our discussion on studies performed on raw bio-liquid upgrading or on model compounds with reacting media mimicking these particular conditions. In this sequence, different catalysts might be used. The first stage process has been investigated using model compounds and crude bio-liquid (top or bottom fractions of a FP bio-liquid) at Groningen or Twente Universities in the screening of supported Ru catalysts [60, 61, 62,63]. This metal is considered to be more active than other noble metals such as Pt and Pd [64] or supported NiCu catalysts [65,66].

Reduced CoMo/Al₂O₃ catalysts were also applied to convert bio-liquids previously pretreated by ozone and H₂O₂ [67]. The condensation reactions in water of eleven different molecules present in the bio-liquid, in the absence of catalysts, were investigated by Hu et al. [68] and demonstrated that polymerization occurs in most cases.

In cooperation with IFPEN, we investigated the impact of time and temperature (200, 250, 300 °C) on the hydroconversion of model compounds (D-glucose, furfural, guaiacol) in water/solvents mixtures over a reduced NiMo/Al₂O₃ catalyst (water content corresponding to the one determined in the bio-liquid) [69]. Then, mixtures of model molecules were prepared and finally a FP bio-liquid was converted. One priority of the work was to establish the C balances. For instance, from GC and HPLC analyses of the products, the following reaction scheme for the catalytic hydroconversion of D glucose was proposed (Figure 8). However, the different analyses performed on the organic and aqueous phases, deposited coke and gas produced allowed identification and quantification of only 50% of the C introduced.

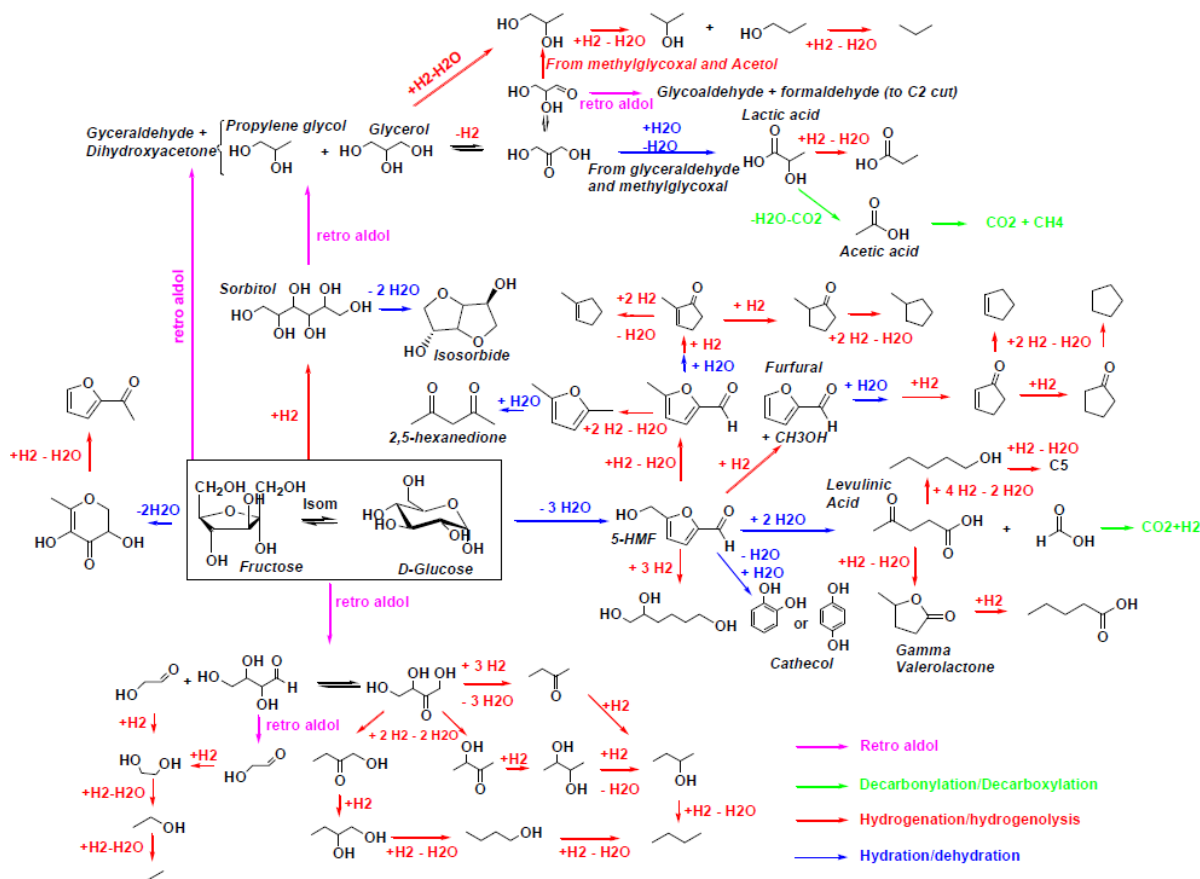


Figure 8. D-glucose catalytic hydroconversion pathways from GC-FID and HPLC-RI analyses. Reproduced from [69].

Size Exclusion Chromatography (SEC) analyses showed the presence of oligomers and FTICR-MS was used to characterize the fraction of the heaviest compounds, as illustrated in Figure 9. 1400 different chemical formulas were detected for molecules containing up to 26 C atoms and 11 O atoms. 93% of the detected compounds have a molecular weight higher than 5-HMF (hydroxymethylfurfural, 126 g/mol). For instance, a compound in the center of Figure 9 with $M_w = 270,24$ g/mol and corresponding to the formula $C_{12}H_{14}O_7$ can be attributed to two different molecules originating from hydration of 5-HMF and its condensation or reaction with another compound.

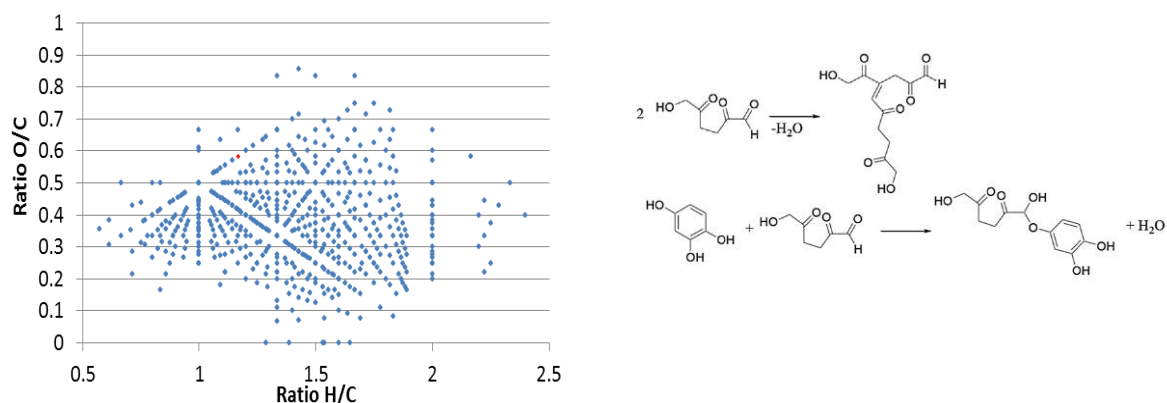


Figure 9. FTICR-MS analysis of D-glucose conversion products and proposed mechanism of formation of a 270.2 g/mol compound. Reproduced from [69].

From this study, it can be assumed that furanic compounds are the **key precursors for the formation of macromolecules**. Furfural reactivity is as complex as D-glucose and leads to macromolecules and solids. The water content has a crucial role on **the formation of solids**. Guaiacol alone **hardly reacts** under these conditions.

When the reacting mixture gained complexity by adding together these components and/or acetic acid, new phenomena occurred. For instance, the addition of guaiacol to D-glucose and furfural led to a large decrease in the production of solids, through solubilization and reaction of **guaiacol with macromolecule precursors, thus preventing condensation**. The contribution of hydrothermal reactions was estimated by the substitution of H₂ by N₂ [70].

When a **fast pyrolysis bio-liquid** (from VTT) was used as reactant, the introduction of guaiacol in the reaction mixture again considerably reduced **the formation of macromolecules**, as illustrated in Figure 10, and prevented carbon deposition [71]. Therefore, C recovery from the bio-**liquid** was increased and the process drawbacks were reduced by introducing solvents.

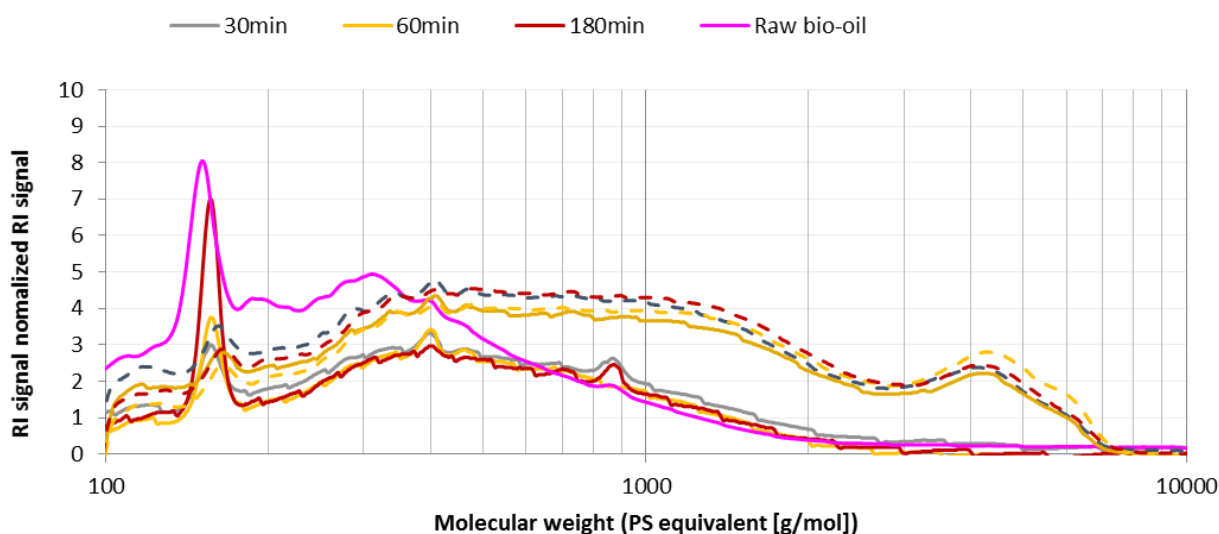


Figure 10. SEC analysis of bio-liquid upgraded at 250°C with guaiacol (50/50 wt.%) (solid lines) or without (dotted lines) versus time, adapted from [70].

Most of the academic studies are using batch systems and estimation of the lifetime and stability of the catalysts is often not addressed. In a cooperative work between PNNL and VTT, continuous-flow units were used to **upgrade** pine bio-**liquids**. The operating conditions were optimized for 100 h tests involving the combination of a Ru-based catalyst in a first stage and sulfide catalysts in a second stage [72]. These tests demonstrated the complete processing to hydrocarbons with a minimal carbon loss in the recovered aqueous phase, but also evidenced catalysts lifetime limitations. Process improvements are still needed.

Hydrotreatments are well established technologies which have been optimized for the conversion of bio-liquids and reached pilot scale developments, for instance in ref [72] (40 cm³ reactor operated at LHSV 0.19 L of bio oil/L of catalysts/h, 400°C, 75-150 bar with Ru/C of Co(Ni)Mo sulfide catalysts). Zacher et al. [73] identified in a review paper the research gaps for the future of bio-liquid hydrotreating research, namely the focus on process integration, the development of appropriate quality metrics for intermediates, the techno-economic analysis and adequation between biofuels and fossil fuels. However, the hydrogen cost in such consecutive processes is a strong economical barrier. Ideally, hydrotreatment should only take place as a finishing process to provide fungible fuels, targeted hydrocarbons or refinery blend-stocks.

3.2. Catalytic steam-reforming of fast pyrolysis bio-liquids

The world demand for pure H₂ amounted to ≈74 Mt in 2018, which is essentially used industrially for ammonia production (42.6%) and oil refining (51.7%) [74]. It is also foreseen since the 2000s as a potential energy carrier, although several drawbacks can be objected such as its low energy density per volume units (it is the lightest existing gas), its high production, transportation and storage costs, and safety concerns in consumer applications related to its wide flammability range combined with very low ignition energy [75]. Hydrogen is currently produced at 96% by steam reforming of fossil fuels (natural gas, coal or oil), which produces 11-12 tons of CO₂ per ton of hydrogen. Therefore, producing syngas and hydrogen from renewable sources such as bio-liquids is an interesting option to mitigate CO₂ emissions.

In catalytic steam reforming (SR) of bio-oils, steam is added as reactant in the feed stream to promote the SR reactions of bio-oil components and the water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) to improve the hydrogen yield. The high H₂O/C ratios (steam is generally added in excess under SR conditions) lead to the formation of essentially H₂ and CO₂, since the light hydrocarbons and the coke that might eventually form are reformed by steam. The WGS equilibrium is also displaced towards H₂ + CO₂ formation in an excess of steam, decreasing the CO content in the effluent stream. In contrast, under gasification conditions no steam is added to the feed and significant amounts of CO, coke and light hydrocarbons are formed (essentially C₁-C₃). However, since bio-oils initially contain 20-30% of water, the bio-liquid components can also react through SR and WGS reactions even though no steam is added.

The pioneer studies on the SR of bio-liquids were published by E. Chornet, D. Montane and S. Czernik in 1995 [76, 77] using model compounds of bio-liquids (acetic acid, hydroxyacetaldehyde, furfural, syringol) and commercial Ni-based SR catalysts. The reforming process was shown to involve gas phase thermal decomposition of the oxygenated compounds followed by steam-reforming of the intermediate products. More complex polymeric components of biomass such as cellulose, xylan, lignin and the aqueous fraction of bio-liquids (which contains essentially low molecular weight compounds derived from cellulose and hemicellulose, such as organic acids, aldehydes, alcohols, ketones, sugars

and a small amount of monomeric lignin-derived phenolic compounds) were also reformed in a specifically designed reactor equipped with a spraying nozzle and three independently heated zones [78]. A large excess of steam was used ($S/C= 20-30$). A stable gas production (composed mostly of CO , CH_4 , H_2 and CO_2) was obtained over 4 hours long experiments, with almost **complete** conversion of inlet reactants into gas products. On the basis of the results obtained with bio-**liquids** model compounds and its aqueous fraction, a regionalized process for hydrogen production was proposed [79], in which small and medium size biomass pyrolysis units provide bio-**liquids** to a large central unit **where hydrogen is produced by SR of the aqueous fraction of bio-liquids, after bio-liquid fractionation and separation of the phenolic compounds to produce resins.**

Feeding crude bio-**liquids** **into** the reactor was identified as a key issue, since bio-**liquids** contain many non-volatile oligomeric compounds and polymerize at low temperature ($\approx 80^\circ C$), clogging the feeding line. Therefore, subsequent studies were performed using model compounds of bio-**liquids** or their aqueous fraction, or the volatile fraction of bio-**liquids** [80]. Different commercial and research Ni-based catalysts underwent a fast deactivation (within 25 min) during the SR of the aqueous fraction of poplar bio-**liquid** at $825^\circ C$, that was related to carbon deposition, but basic additives such as MgO and La_2O_3 were found to decrease the extent of carbon deposition, **whereas N-Co and Ni-Cr promoted catalysts were found the best research catalysts** [81]. The catalysts could also be regenerated by coke gasification under steam or CO_2 . A much better catalyst stability (over 90 h) was obtained during SR of bio-**liquid** aqueous fraction in a fluidized-bed reactor operated at $850^\circ C$, using a commercial Ni-based naphta reforming catalyst (**C11-NK from Süd-Chemie, ground and sieved for fluidization and containing Ca, Mg and Si additives**) [82]. The reactor temperature was an important parameter in the coke deposition process, since at $800^\circ C$ a slow catalyst deactivation was observed.

The aqueous fraction of bio-**liquids**, however, does not represent the complexity of crude bio-**liquid** composition, notably the high molecular weight compounds derived from cellulose, hemicellulose and lignin. Therefore, the following section will focus specifically on SR studies performed using crude bio-**liquids** and the reactor concepts developed for this purpose.

The first steam-reforming experiments using a crude bio-**liquid** appear to have been reported by Rioche et al. in 2005 [83]. The bio-**liquid** was dripped by gravity on top of a catalyst bed heated at $740-860^\circ C$ under a high steam/carbon ratio (10.8) and the water droplets were used to carry away the bio-**liquid** droplets into the reactor. The catalysts were 1 wt.% Pt or Rh deposited on Al_2O_3 or ceria-zirconia supports. Since the water and bio-**liquid** feeding was not strictly continuous, the reactor effluents showed periodic composition fluctuations with time, but a reasonably stable H_2 yield $>50\%$ was obtained at $830^\circ C$ over 9 h using the $Pt/(CeZr)O_2$ catalyst, with a carbon yield (into CO , CO_2 and CH_4) around 90%. Significant carbon deposition on the catalyst was reported but not quantified.

In 2007, Czernik et al. [84] succeeded in producing syngas from a crude bio-**liquid**, mixed with 10% methanol to homogenize the **liquid** and reduce its viscosity, in a fluidized-bed reactor with a H_2 yield of $\approx 70\%$. Different Ni-based SR catalysts were developed and a

temperature-controlled injection nozzle was used to spray bio-liquid droplets on the catalyst. The catalysts, however, deactivated slowly over 10-18 h time on stream.

Domine et al. [85] also investigated the SR of a crude bio-liquid, prepared from beech wood, using Pt/Ce_{0.5}Zr_{0.5}O₂ and Rh/Ce_{0.5}Zr_{0.5}O₂ catalysts supported on cordierite monoliths. To prevent polymerization of bio-liquid in the feeding line, a double envelope stainless steel tubular reactor equipped with water-cooling was designed that allowed injecting the bio-liquid through a capillary on top of the hot fixed-bed reactor while keeping the bio-liquid below 50°C. At a H₂O/C ratio of 10 and a catalyst temperature of 780°C, the bio-liquid conversion was total and the H₂ yield reached 70% with Pt/Ce_{0.5}Zr_{0.5}O₂, but only 52% with Rh/Ce_{0.5}Zr_{0.5}O₂. This was attributed to the higher activity of Pt in the WGS reaction. The hydrogen productivity reached 49 mmol H₂/g_{bio-liquid} at S/C=10 and 780°C. About 12 wt.% of coke was deposited on both catalysts after 1.5 h on stream, but it did not result in a change in the reactor effluent composition over this duration, probably because the carbon deposition remained limited at the monolith channels inlet and did not poison the catalyst washcoat downstream in the channels. This coke could be removed under 20% O₂. The high temperature combined with high steam concentration, however, led to a ≈60% decrease in the catalysts surface areas after the SR tests.

Similarly, van Rossum et al. [86] compared the thermal and catalytic SR of crude bio-liquids, synthesized from beech or pine woods, in a pilot-scale fluidized bed reactor. In the non-catalytic runs, the fluidization medium was sand, whereas catalytic runs used two different KATALCO commercial catalysts (K23 and K46) optimized for methane or naphta reforming, respectively. The thermal reaction of bio-liquids produced essentially CH₄, CO and C₂-C₃ hydrocarbons but also liquid products, and the H₂ yields were low (10-15%). The catalysts improved strongly the hydrogen yields (40-46%) by fully reforming the methane and light hydrocarbons into syngas. However, a rapid catalyst deactivation took place within the first hour of operation (≈25% in H₂ production rate), but the catalyst activity was not recovered after carbon burn off, leading to the conclusion that this deactivation was related to an irreversible catalyst evolution and not to carbon build-up.

The set-up was modified for a two-stage configuration, in which the bio-liquid was first thermally pyrolysed in the fluidized bed reactor over sand, while a fixed bed reactor containing K23 and K46 catalysts was added immediately after the fluidized bed to convert the gaseous products. In this configuration, a stable reactor operation was obtained over 11 h with a H₂ yield of 68% (Figure 11). The staged gasification/steam reforming unit was further optimized as regards its operating conditions (gasification temperature, S/C ratio) [87]. The temperature in both the fluidized bed reactor (432-788°C) and fixed bed reactor (533-828°C) had no influence on the total carbon recovery, defined as the % of carbon converted to permanent gases. The temperature of the fluidized bed could be lowered to 500°C to function as a bio-oil evaporator rather than a gasifier, leading to less cracking of bio-oil vapors into CH₄ and C₂-C₃ hydrocarbons. This was beneficial to the fixed bed unit since the SR catalyst appeared to be more active to convert directly the bio-liquid vapors than methane and light hydrocarbons. However, the fixed bed reactor temperature could not be lower than 700°C to prevent excessive carbon deposition. The impact of the inlet H₂O/C

ratio on the outlet H_2/CO ratio agreed with the calculated equilibrium compositions, suggesting that the catalyst was also active for the WGS reaction.

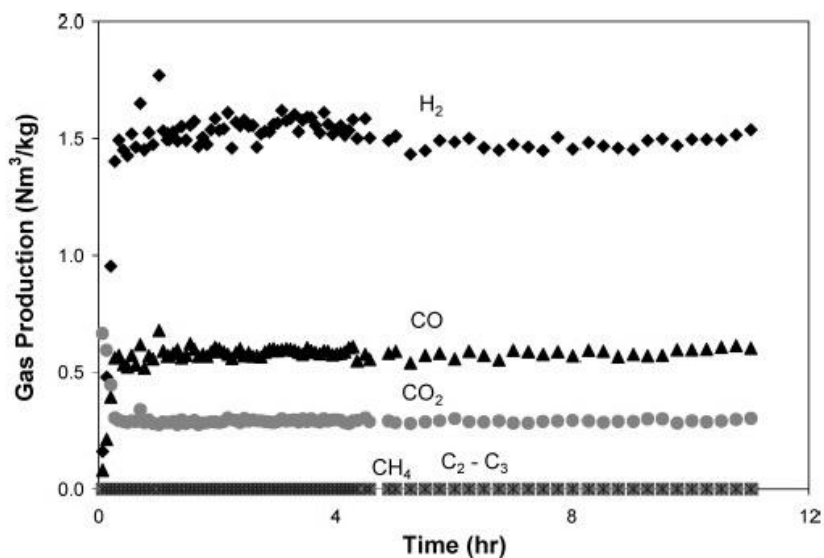


Figure 11. Gas production from pyrolysis liquid gasification and SR in two beds in series (fluidized bed: $T=805^{\circ}C$, SR bed: $T=815^{\circ}C$, $S/C=1.5$). Reproduced from [86].

Anticipating heavy coke deposition, Wu et al. [88] processed a crude bio-liquid in a two-stage fixed-bed reactor system, in which the first reactor ensured a primary steam-reforming over an inexpensive Dolomite catalyst (whose deactivation due to coke deposition was considered acceptable), while in the second SR reactor a NiO/MgO catalyst was used for secondary SR of the primary gaseous effluents exiting from the first reactor. The bio-liquid feeding line was kept at controlled temperature ($50^{\circ}C$) to prevent polymerization. Liquid products were condensed at the first reactor outlet and only the gaseous products were sent to the second reactor. Under optimal operating conditions ($900^{\circ}C$, $S/C=12$ and 16), the carbon selectivity towards gas products (CO , CO_2 and CH_4) reached 80.1%, whereas 7% of the inlet bio-liquid carbon was converted into coke deposits in the first reactor, and 12.9% was converted into liquid products. The second reactor ensured essentially the SR of methane, which was converted at 96% at $800^{\circ}C$ under $S/C=2-4$, therefore improving the H_2 yield to 81%. However, carbon deposition in the second reactor was not fully prevented since carbon whiskers were observed on spent NiO/MgO catalyst, although in lower amounts (1.97%-0.52 % at $700-900^{\circ}C$) than in the first reactor. These carbon whiskers are probably formed by the Boudouard reaction or by CH_4 cracking reactions.

Similarly, this dual-bed concept has been applied later to a fixed bed reactor using first a sand bed to gasify the crude bio-liquid followed by a NiCuZnAl catalyst to reform the vapors [89]. The H_2 yield was close to 65%, and was improved to 81% when the reforming reactor was implemented in an original electrochemical catalytic reforming mode, in which an annular Ni-Cr wire was heated electrically to provide the required heat to the NiCuZnAl reforming catalyst. Although the promoting effect of the electric wire was not fully

understood, it significantly reduced the amount of carbon deposited on the reforming catalyst, compared to the reforming process with furnace heating.

Since then, several reviews on the SR of bio-liquids have been published [90, 91, 92, 93, 94, 95]. The main features emerging from the literature reviewed are summarized below:

- Bio-liquids are a difficult feedstock for catalytic SR reactors: due to polymerization at low temperature, the temperature of the bio-liquid feeding line must be carefully controlled.
- Due to the thermal instability of bio-liquids and to the high temperatures required for SR reactions, the thermal decomposition of bio-liquid components is the primary reaction pathway. The catalysts promote the SR of light compounds (hydrocarbons and oxygenated compounds) and the WGS reaction, which strongly improves the syngas yield compared to thermal reactions.
- The first cause of catalyst deactivation is coke deposition. Monolith catalysts and fluidized bed catalysts provide a better control of carbon deposits and of catalyst deactivation. The catalyst formulation can be adapted to reduce the coke deposition by promoting carbon gasification with steam. However, the high temperature and the presence of steam also favor catalyst sintering and deactivation.
- Reactors with dual bed configurations also allow a better control of coke deposition: in a first reactor a sacrificial solid (sand or other low cost solid) receives main part of the coke formed by deposition of the heavy compounds present in the bio-liquids, therefore protecting the reforming catalyst placed downstream in the second reactor.
- Online SR reforming of pyrolysis vapors (directly after the fast pyrolysis reactor) appears an interesting option, since it eliminates the issues related to bio-liquids handling and feeding in a SR reactor. However, in this configuration the SR catalyst is more directly exposed to the biomass components (mineral and sulfur compounds) that can induce catalyst deactivation.

3.3. Catalytic cracking/gasification of bio-liquids

Producing syngas and hydrogen from renewable sources represents a valuable option to mitigate CO₂ emissions. Biomass can be gasified directly to produce syngas, but industrial gasifiers are complex units that require careful operation control and technical maintenance and are not well adapted to small scale and decentralized production. Gasifying biomass, therefore, requires costly transportation logistics of biomass feedstocks to centralized gasification units. In contrast, fast pyrolysis of biomass can be easily implemented as small decentralized units, where biomass is available to produce bio-liquids. Bio-liquids have a higher energy density than raw biomass and are easier to transport, they contain less mineral impurities, which are an issue in a gasifier, and they can also be gasified, without any steam addition in the feed, to produce syngas or hydrogen.

The first studies related to bio-liquids gasification were reported by IRCELYON in 2007-2008. Anticipating heavy coke deposition due to the high content of aromatic and oligomeric

compounds in bio-liquids, a two-steps sequential process was proposed, in which the crude bio-liquid was cracked on Ni-based catalysts followed by catalyst regeneration under air to burn the deposited coke [96]. In addition, burning the coke in a separate step offers the possibility of capturing the CO₂ emitted. The bio-liquid was fed in the reactor using a syringe pump and a stainless-steel capillary connected on top of the catalyst bed. To prevent bio-liquid polymerization and capillary clogging, a dedicated stainless-steel reactor equipped with a water-cooled nozzle was designed to keep the bio-liquid below 50°C at the reactor inlet, while the catalyst was heated at 700°C in the reactor.

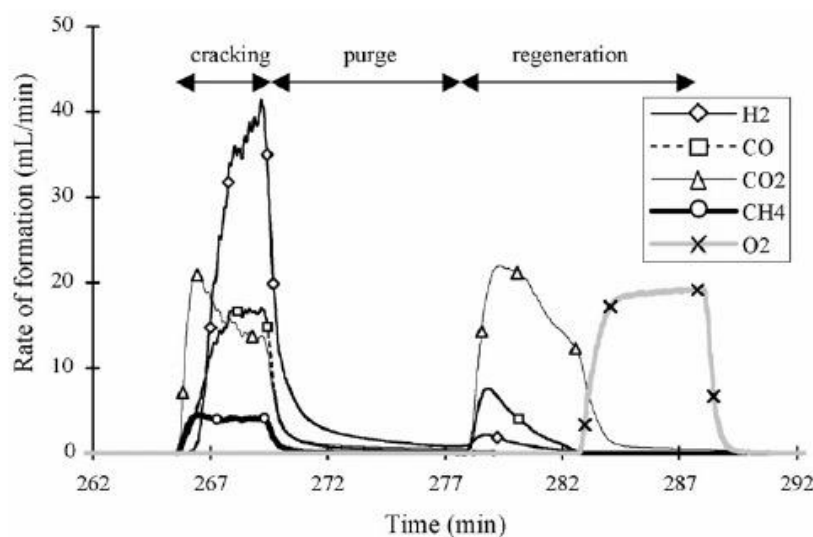


Figure 12. Gaseous products formation during a single cracking/regeneration sequence on Ni-K/La₂O₃-Al₂O₃ catalyst. Conditions: 600 mg catalyst, T = 700°C, cracking: 5 mL/min bio-liquid in 100 mL/min Ar; regeneration: 20% O₂ in Ar, total flow rate 100 mL/min. Reproduced from [96].

During the cracking step, the gaseous products consisted in H₂ (49.2%), CO (25.2%), CO₂ (18.2%) and CH₄ (7.3%). During the catalyst regeneration, essentially CO₂ and minor amounts of CO and CH₄ were formed. The carbon balance closure was 95% in the cracking/regeneration sequence, the deficit corresponding to carbon deposition on the reactor walls and on the thermocouple placed in the reactor. A reproducible outlet reactor composition was observed over 12 cracking/regeneration sequences. Comparison of Ni/Al₂O₃ and Ni-K/La₂O₃-Al₂O₃ catalysts with the thermal cracking of bio-liquid revealed that the catalysts promoted the gasification of bio-liquid and improved the syngas yield through steam-reforming and WGS reactions involving the water contained in the bio-liquid. The removal of coke during the regeneration was also effective at lower temperature in the presence of catalysts, particularly with the Ni-K/La₂O₃-Al₂O₃ catalyst. The coke deposits were also different on the two catalysts: large amounts of carbon whiskers bearing Ni particles at the tip were observed on coked Ni/Al₂O₃ catalyst, whereas essentially amorphous coke was found on Ni-K/La₂O₃-Al₂O₃. This led to a significant loss of Ni (\approx 9%) after 12 cracking/regeneration sequences over Ni/Al₂O₃, since the Ni particles were flushed away during the combustion of the carbon whiskers, while the Ni content remained unchanged in the Ni-K/La₂O₃-Al₂O₃ catalyst.

Using two parallel reactors working alternately and acetic acid as bio-liquid model compound, continuous syngas production was demonstrated [97].

The cracking of crude bio-liquids was also performed over Pt/Ce_{0.50}Zr_{0.50}O₂ and Rh/Ce_{0.50}Zr_{0.50}O₂ catalysts, tested as powder or as structured catalysts (deposited on cordierite monoliths) [98]. The Pt/Ce_{0.50}Zr_{0.50}O₂ revealed a significant deactivation along the cracking/regeneration sequences, whereas the Rh/Ce_{0.50}Zr_{0.50}O₂ performances were more stable. Monolithic catalysts also exhibited a higher stability than powder catalysts, which was related to a better gasification of soot deposits and to an improved conversion of the small molecules formed by thermal cracking of the bio-liquid. During cracking steps with durations of 10 to 15 min, the reactor effluents contained ≈50% H₂. The oxygen storage properties of the ceria-zirconia support improved the gasification of soot deposits and the catalyst regeneration. Reaction enthalpy calculations for the cracking and the regeneration steps showed that enough heat was generated by combustion of the coke deposits to compensate for the heat required in the endothermic cracking step. The overall bio-liquid cracking pathway involved thermal decomposition reactions into primary products that were further converted into syngas through catalytic steam-reforming and WGS reactions, which result from the initial water content (30 %) present in the bio-oil (Figure 13).

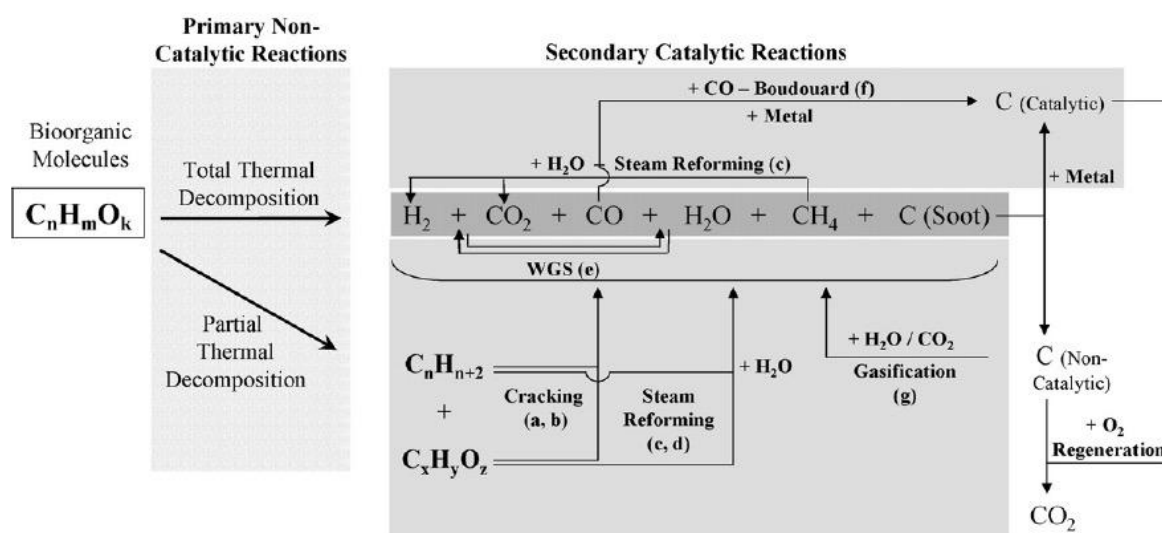


Figure 13: Proposed reaction pathway for the sequential cracking of bio-liquid. Reproduced from [98].

Jiang et al. [99] also investigated the catalytic cracking of the light fraction (Bp 105-115°C), obtained by distillation, of a crude bio-liquid produced from rice husk, using 20 wt.%Ni/Al₂O₃ and 5 wt.%Ce/HZSM-5 catalysts, to produce syngas. The bio-liquid was mixed with water (water/liquid mass ratio of 3), which actually qualifies the reaction as steam reforming rather than cracking. Compared to the thermal reaction, both catalysts significantly enhanced the bio-liquid conversion, but the 20 wt.%Ni/Al₂O₃ catalyst produced essentially H₂ (66%) and CO₂ (31.7%) whereas the 5 wt.%Ce/HZSM-5 catalyst produced mostly C1-C4 alkanes and alkenes (43.8%), CO (24.6%), CO₂ (23.5%) and little H₂ (8.1%).

Clearly, 20 wt.%Ni/Al₂O₃ catalyzed the SR and WGS reactions, whereas 5 wt.%Ce/HZSM-5 catalyzed cracking reactions leading mainly to the formation of light hydrocarbons and olefins.

4. Co-processing of bio-liquids with feeds from refineries: hydrotreating, fluid catalytic cracking, hydrocracking

Existing oil refineries offer a unique opportunity to integrate pyrolysis liquids by co-processing with refinery feeds using well-established petroleum technologies. Unfortunately, FP liquids are poorly miscible in conventional fuels and a pretreatment to reduce the oxygen content, ideally below 20 wt.%, is required.

A review on the refining units and the technical and economical possibilities for co-processing were proposed by Talmadge et al. [100]. IRCELYON has been long involved in this aspect, through EU programs and collaborations with IFPEN. Co-processing by FCC or by hydrotreatment were the most investigated refinery processes. Our activity in these two domains will be summarized hereafter.

Co-processing of bio-liquid with Vacuum Gasoil (VGO) in a Fluid Catalytic Cracking.

Large production of renewable transportation fuels is very challenging, implying that for rapid change existing infrastructures should be used and that the same quality of the final fuels should be guaranteed. A realistic scenario for bio-fuels mass production in the short term is to consider "co-processing" of biomass-derived resources together with conventional crude oil in standard refineries.

Pyrolysis-liquids obtained from fast pyrolysis of lignocellulosic biomass are among the best candidates for co-processing, since they present physico-chemical and rheological similarities with crude petroleum feeds, while the technology for producing them is commercially available [101]. However, their lower heating value, immiscibility with hydrocarbon fuels, chemical instability, high viscosity and corrosiveness, deriving from their high oxygen content make co-processing of "crude" pyrolysis liquids a challenge. Therefore, to make them compatible with petroleum feedstocks, various upgrading processes have been investigated, among which hydrodeoxygenation (HDO) to reduce the acidity and the oxygen content of raw bio-liquids before their co-processing.

Fluid catalytic cracking (FCC) is a key process in a modern oil refinery mainly because of its flexibility it can respond to fluctuations in feedstock and product demands. Its principal function is to convert high molecular weight hydrocarbons obtained from crude oil distillation into more valuable products, mainly gasoline, light cycle oil (LCO) and propylene. A typical distillate feedstock used in FCC is vacuum gasoil (VGO) or long-residue (LR). Catalytic cracking is rather well suited for the conversion of pyrolysis liquid, because, while the large molecules in the pyrolysis liquid are being cracked, oxygen is removed at the same time through dehydration, decarboxylation and decarbonylation. Meanwhile, the co-processing of pyrolysis liquids, even in small quantities, can have an impact on the quantity and quality of the FCC products. Catalytic cracking proceeds through a complicated reaction

mechanism with a large number of reactions involving a huge number of different molecules. FCC catalysts and additives are fine-tuned to get the optimal yields for the desired product slate. Introducing oxygenates into the feed that have strong interactions with the catalyst can thus alter the product distribution. Especially the coke production is concerning as a FCC unit is heat balanced through coke combustion.

A number of reviews summarize the progress of co-processing pyrolysis liquids with refinery fossil petroleum feeds in FCC lab-scale and demo units during the last decade [102, 103, 104, 105, 106]. Bezergianni et al. [107] list 18 co-FCC studies for pyrolysis liquid in their review on refinery co-processing of renewable feeds, including 4 studies on pilot or demo scale, showing the interest of the petroleum industry for this technology. Lappas et al. [108] were one of the first to test the concept of co-processing in a pilot scale circulating riser reactor. They successfully co-processed the heavy fraction of lightly hydrogenated beech wood pyrolysis liquid with LCO (light cycle oil) and VGO. Almost all studies report the feasibility of co-processing small amounts (< 20 wt.%) of pyrolysis liquids, sometimes without any upgrading, with usually only small changes in the product distribution. Hydrogen transfer from the petroleum feed to the bio-liquid components is usually reported as the synergetic effect, making the co-processing feasible compared to the catalytic cracking of pure pyrolysis liquid that usually results in large coke production.

Refinery co-processing studies, both hydrotreating and FCC, at IRCELYON started within the framework of the European Biocoup project [109]. Co-FCC experiments were carried out in a fixed bed reactor of the microactivity type (MAT). Typically, a reaction cycle consisted of 30- 60 seconds cracking at 500 °C – 560°C, 15 - 20 min of stripping under inert gas flow, 40 - 60 min regeneration under 20 vol.% of O₂ at 650 °C and 5 - 15 min purge. The liquid feed rate was varied to obtain different catalyst to oil ratios (Cat/Oil). During the cracking and stripping steps, the liquid product was collected in a glass receiver located at the exit of the reactor and kept at -50 °C. Meanwhile, the gases were collected in a gasbag or burette. The amount of coke formed on the catalyst was estimated from the carbon dioxide production during the regeneration period.

In the first experiments, HDO liquids and VGO were mixed together and kept in a storage vessel at around 60°C under constant stirring during the experiment. This mixture was then fed to the reactor with a single pump. This resulted in significant fluctuations with respect to the amount of HDO liquid injected into the reactor. Therefore, two liquid feed systems were set-up, one for VGO and one for pyrolysis liquid, each with heated vessels and heat-traced transfer lines. A similar modification was done later on the MAT reactor from PID Eng & Tech.

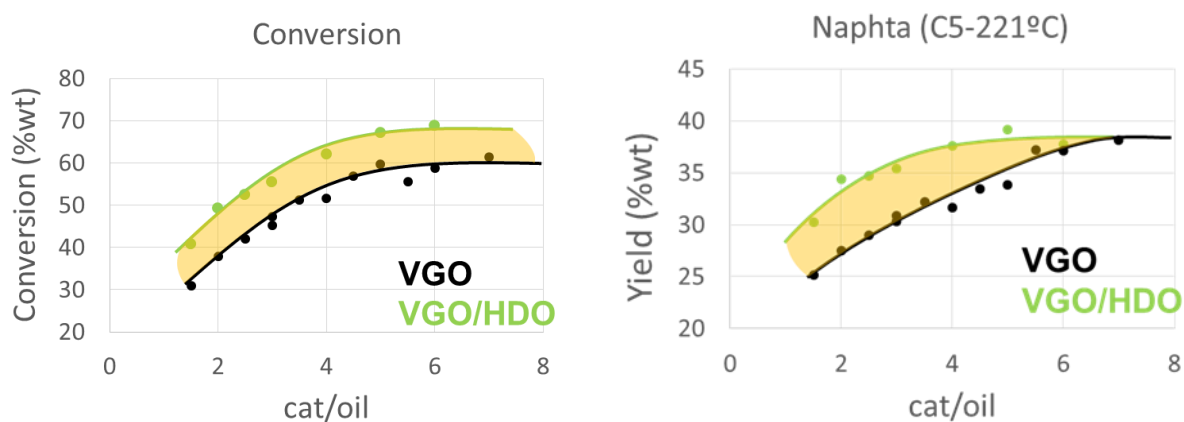
Before investigating the effect of co-feeding pyrolysis liquid with VGO, studies using oxygenated model compounds were co-fed with isooctane over an equilibrated FCC catalyst (e-cat) at a 2 wt.% level. Addition of an oxygenated compound, regardless of its nature, resulted in lower conversions of isooctane cracking and impacted the product distribution significantly [110]. The effects found in this study were much more dramatic than the effects found in co-processing VGO with fast pyrolysis liquids, implying that one should be rather careful of extrapolating results from model component studies to more complex feeds.

Initial experiments focused on co-processing of 10-20 wt.% of the bottom fraction of pyrolysis liquid (from pine wood) following an HDO step, typically having an oxygen content

of around 20 wt.%. VGO/HDO-oil co-processing produced slightly higher dry gas yields and coke, lower LPG yields while gasoline and LCO yields are comparable to those of the cracking of VGO. A typical example of these co-processing experiments is given in Figure 14, where processing of VGO is compared to co-processing of a 90 wt.% VGO/10 wt.% HDO liquid. During co-processing oxygen removal from HDO-liquid oxygenates consumes hydrogen, as the majority of the oxygen is removed by dehydration. This hydrogen is supplied by hydrocarbon cracking through hydrogen transfer reactions. As a result, the final product composition is poor in hydrogen and contains more coke, aromatics and olefins [111, 112]. Moreover, the phenolic fraction (alkyl-phenols) was not converted completely in agreement with the findings of De Miguel Mercader et al. [113, 114].

A more detailed analysis of coke formation indicated a large diversity of coke deposits and their location [115]. Two routes for coke production were proposed: one based on the fossil hydrocarbon route as proposed earlier by Guisnet and Magnoux [116] blocking Bronsted acidity inside the micropores. The second route is the conversion of large lignin oligomers assumed to proceed in the outer volume of the mesopores [36]. Carbon 14 analysis showed that a higher fraction of the initial ^{14}C ends up in the coke, but the fossil fraction increased even more during co-processing attributed to the increased aromaticity by hydrogen transfer reactions [117].

The hydrogen consumption during the HDO is high and makes the process economically unattractive. Full HDO might not be required when the pyrolysis liquid is being co-processed. Therefore, recently a series of partly hydrogenated liquids were used for co-processing and the resulting liquid products were analyzed in detail. Figure 15 shows the oxygen content of the upgraded liquid as a function of the hydrogen consumption. Initially a consumption of hydrogen is observed, but the oxygen content remains constant, followed by a moderate H_2 consumption, but a rapid increase of the degree of deoxygenation. The first process is likely the transformation of aldehydes into alcohols, a reaction that consumes hydrogen but does not change the O/C ratio. Co-processing of the series of upgraded liquids showed a trend with the oxygen content with an optimum around 150-200 NL H_2/kg . Analysis of the gasoline quality also showed an optimum at these values, as represented by the octane number [118].



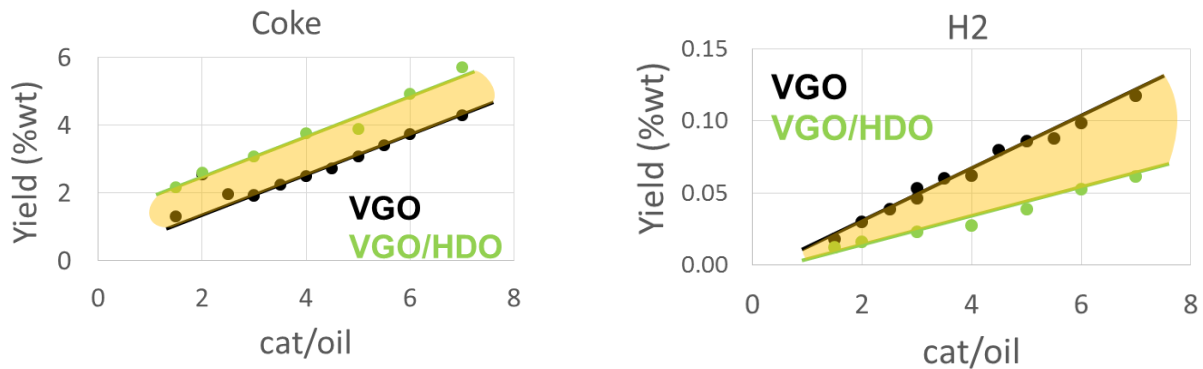


Figure 14. Conversion (top left) and yields of naphtha (top right), coke (bottom left) and hydrogen (bottom right) during co-processing of 10 wt.% HDO liquid with VGO as a function of the catalyst to oil ratio. Black symbols pure VGO cracking; green symbols 10/90 wt.% HDO liquid/VGO coprocessing.

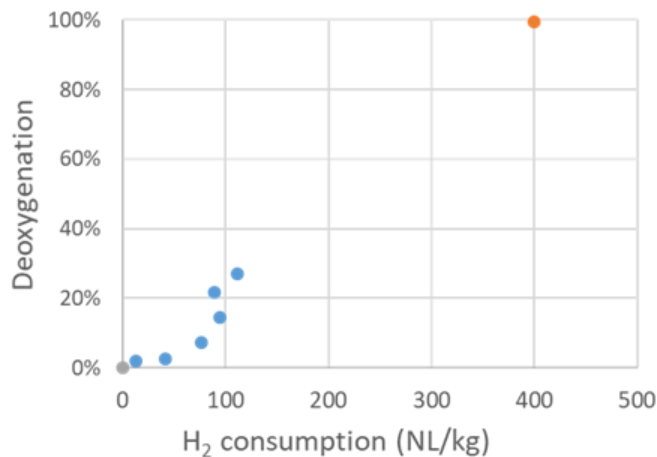


Figure 15. Degree of deoxygenation of pyrolysis liquid as a function of the hydrogen consumption during the HDO step.

These results indicate that only partial hydrogenation of the pyrolysis liquid is necessary in order to stabilize the pyrolysis liquid.

Catalytic pyrolysis liquids were produced by addition of ZSM-5 during the fast pyrolysis. These catalytic pyrolysis liquids were co-processed directly without any further upgrading. Gasoline yields were similar to pure VGO cracking, but the gasoline contained much more aromatics. The organic yield of the catalytic pyrolysis route was estimated at 30 wt.%, compared to an overall yield for the HDO of 24 wt.% [119]. Catalytic pyrolysis thus offers an interesting route for the production of bio-fuels via co-processing in a FCC unit.

To summarize, co-processing of pyrolysis liquids in FCC units seems a promising route to introduce renewable carbon into refinery products. Catalytic cracking in the presence of a petroleum feed is an efficient process for removing oxygen from the pyrolysis liquid, through hydrogen transfer reactions. However, mechanistic details are still lacking and the impact of the oxygenated compounds on the different reaction families during catalytic

cracking is still largely unknown. The pyrolysis liquids do not need to be deoxygenated to a large degree, but stabilization of the liquid by removing the most reactive functional entities is necessary. This can be accomplished by either mild hydrogenation or by catalytic pyrolysis. Co-processing fast pyrolysis liquids up to 10 wt.% hardly effects the FCC yields. Higher amounts have a negative effect on the overall FCC process, mainly by higher coke yields. Due to the tremendous throughput of an industrial FCC unit, pyrolysis liquids will be fed at less than 5 wt.%. The co-FCC lab results are largely in line with large scale testing results such as those reported in [120].

Co-processing hydrotreated bio-liquids in hydrodesulfurization units

Co-processing vegetable oils with crude oils for the production of diesel or jet fuels is well established in industrial processes, such as NexBTL, Ecofining, Vegan or H-Bio processes. In the latter case, the vegetable oil is co-processed with a Straight Run Gas Oil (SRGO), the triglycerides providing alkanes that improve the cetane index [121]. However, these processes are hardly competitive since the cost of vegetable oils is detrimental, and their commercialization is related to the regulation on biofuels and the mandatory introduction of such fuels in kerosene (or diesel).

As an alternative, bio-liquids obtained from fast pyrolysis of biomass have been considered in order to incorporate renewable sources in diesel fuels [122]. The interest resides in the relatively low cost of these bio-liquids. However, as compared to triglycerides, these liquids present chemical and physical characteristics that hardly fulfil the requirements of conventional refining units. As described in the previous sections, they require deoxygenation through a preliminary hydrogenation step. Considering the economical aspect of biofuels production, the use of existing refining units, either FCC or HDT, might be a valuable option to introduce renewable liquids in fuels. The existing capacity of HDT units, which convert more than 50 Mb/day, offers a strong facility to introduce biomass in fuels. Half of the products of a refinery have been converted in an hydrodesulfuration (HDS) unit, either to fulfil the stringent requirement of S content in fuels or to protect downstream catalysts. The present section will focus on the HDS/HDO coprocessing.

Catalytic hydrotreatment takes place at high temperature under hydrogen pressure. The operating conditions are highly dependent on the impurities and the feedstock. Concerning gas oil, hydrotreatment is conventionally carried out on sulfide catalysts between 15 and 110 bar at temperatures ranging from 320°C to 400°C. These conditions can be also used to perform HDO reactions (C-O bond rupture), and therefore the coprocessing of hydrogenated bio-liquids with a SRGO might be a relevant way to convert renewables into fuels. However, the goal of HDS is to provide fuels fulfilling the legislation in the Europe Union of 10 ppm S in gas oil, while this drastic requirement should be achieved whatever the addition of renewable compounds in the feed. Thus, co-processing hydrotreated bio-liquids and SRGO can be envisaged only if the competition between HDO and HDS reactions can be easily overcome by process adjustment.

Straight run gas oils are obtained by atmospheric distillation of crude oils and constitute the main source of gas oil in the refinery. This gas oil cut corresponds to a distillation range of about 230-380°C. SRGO's have a relatively high content of paraffins and naphthenes, and a medium aromatic content (25-40 wt.%). Hydrotreating reactions on a SRGO, processed under hydrogen pressure, eliminate heteroatoms and perform hydrogenation reactions. In principle, few cracking reactions are observed and the initial carbon distribution is preserved after the process. During the heterogeneous catalytic process, hydrogen dissociates on the sulfide catalyst and reacts with the C-X (X = heteroatom: S, O, N) or C=C bond of the adsorbed molecule. The catalyst selection **could** favor one or another of the **above mentioned reactions** occurring during the **process**. Therefore, when **bio-liquid** is mixed with an SRGO, HDT catalysts can perform HDO simultaneously with HDS (or **hydrodenitrification, (HDN)**). This can lead to a substantial increase in hydrogen consumption but also to **undesired** inhibition, which could increase the S content in the product.

Considering the composition and properties of bio-**liquids** [123], **which can be partly controlled by process modifications such as multi-stage condensation or hot gas filtration**, it is well recognized that a first catalytic step is required for stabilization and water abatement [124]. After this first more or less severe hydrotreatment step of the starting bio-**liquid**, the organic fraction further used in this study still **contains** a large number of oxygenates, essentially different families of phenols, as will be illustrated later on. Therefore, **deep** HDO is required to obtain oxygen-free hydrocarbons. Similarly to HDS, the conversion of phenolic compounds leads to two different pathways, namely direct deoxygenation route (DDO) or hydrogenation route (HYD) [125, 126, 127], and the catalyst design **can** significantly drive **hydrodeoxygenation reactions** towards one pathway or the other [128].

In contrast with H₂S, which inhibits HDS and HDA reactions, the water formed during the reaction has a moderate or **no** inhibiting effect on the hydrodeoxygenation rate of phenolic compounds [126, 129, 130] or **coal derived kerosene oil** [131]. **These effects have been described** by theoretical calculations on promoted and unpromoted **sulfide catalysts** [132].

Competitive experiments between S and O containing compounds were performed in the early 80's in the framework of the valorization of coal **liquids** which contain O compounds. Thus, it was demonstrated that the hydrodeoxygenation of a single-ring alkyl phenol, m-cresol, on a CoMo/Al₂O₃ catalyst is inhibited by **benzothiophene (BT)** and dibenzothiophene (**DBT**) (reaction conditions: 375°C-400°C, 69 atm H₂). Oxygenated compounds typical of bio-**liquids**, such as guaiacol and phenol, also inhibited the transformation of refractory **4,6-DMDBT** (and DBT) on CoMoP/Al₂O₃ catalyst. Both reaction pathways (HYD and DDS) involved in the HDS of 4,6-DMDBT and DBT are similarly inhibited, due to competitive adsorption of the oxygen and sulfur-containing compounds on the catalyst surface, which follows a Langmuir-Hinshelwood model [133].

From these model molecules studies, **it appears that** HDO and HDS compete on the same adsorption sites and that inhibition will occur in the co-processing process. Characteristic molecules from coal-derived **liquids** such as dibenzofuran are the most

refractory compounds for HDO and dibenzofuran is the strongest competitor with HDS. However, this molecule is not present in bio-liquids.

In the framework of the Biocoup program, as a preliminary approach to co-processing, we have studied the introduction of a model molecule, guaiacol, as representative of the oxygenated compounds found in hydrotreated bio-liquids [134]. This molecule is interesting since it exhibits both phenol and methoxy groups. Catalytic hydrotreatment tests were performed, for several days, in a trickle-bed reactor described in [135]. The feed was a SRGO (13500 ppm S) crude or spiked with 5000 ppm of guaiacol. The result of this coprocessing is illustrated in Figure 16. An inhibition of the desulfurization reaction was observed at short contact times, which slowly disappeared when the reaction temperature was increased. As soon as Ultra Low Sulfur Diesel (ULSD) conditions were reached at 360°C (or 340°C and LHSV 1h⁻¹), no more inhibitions were observed. This clearly indicates the simultaneous adsorption of S and O compounds, which compete for the same catalytic sites. However, when high HDS and HDO conversion rates are achieved under ULSD conditions, only refractory 4,6-DMDBT remained while oxygenated compounds were fully converted. Comprehensive GCxGC MS was very useful to characterize and to monitor the products of guaiacol conversion within the complex gas oil matrix. We showed that guaiacol was rapidly converted into phenol and methyl phenols compounds, which were also further deoxygenated.

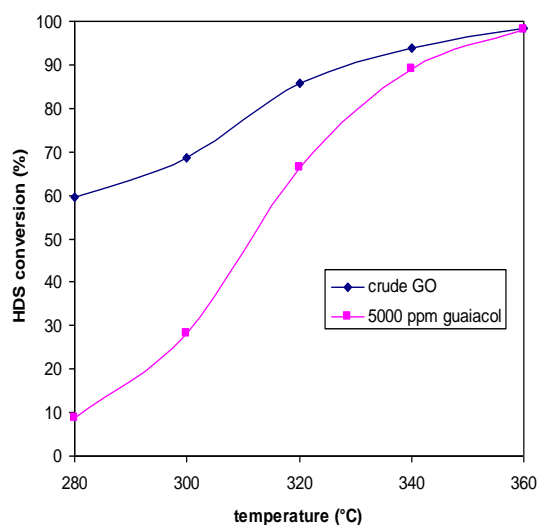


Figure 16. HDS conversion of SRGO and SRGO + guaiacol versus temperature (LHSV 2 h⁻¹, 4 MPa), from Ref. [134].

In fact, guaiacol conversion follows a complex reaction scheme involving several reaction pathways: demethoxylation (DMO), demethylation (DME), DDO, HYD, methylation and condensations, leading to a complex reaction scheme [134]. These products were identified by GCxGC MS, as illustrated in Figure 17.

After co-processing, the absence of catalyst deactivation due to the presence of oxygenated molecules was evidenced by full recovery of the performances in the conversion of pure SRGO.

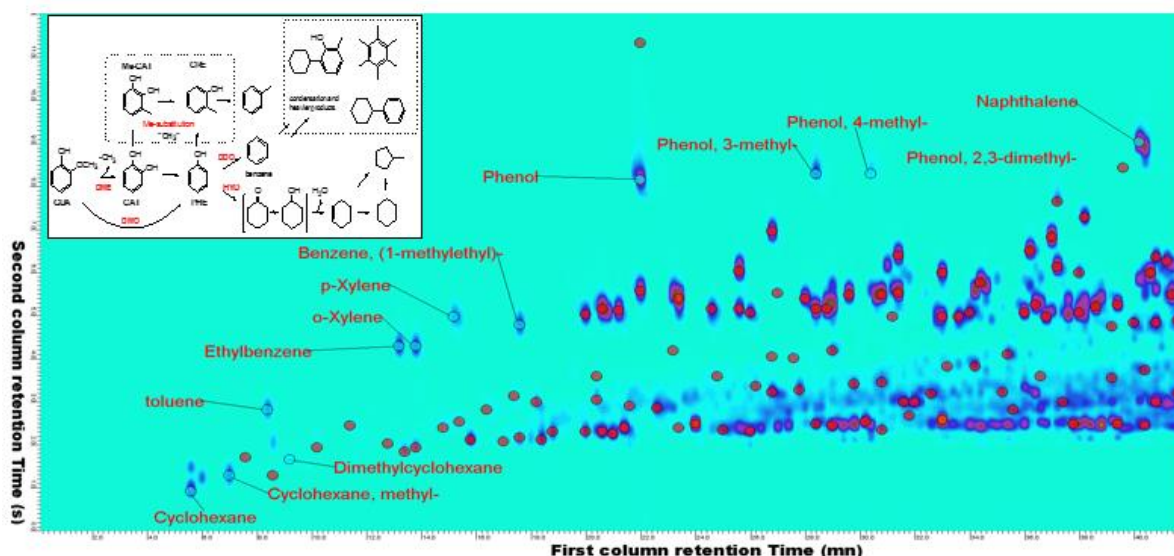


Figure 17. Enhanced view of the volatile compounds region in a GCxGC MS chromatogram (TIC) after conversion at 300°C, and guaiacol HDO reaction scheme (adapted from ref [134]).

In another study performed at IFPEN, a series of oxygenated compounds were co-processed with a SRGO containing 1.35 wt.% S in a pilot unit over a sulfided commercial CoMo/ γ Al₂O₃ hydrotreating catalyst [136]. Runs were performed for several weeks, the main reaction conditions being 330 °C, 1h⁻¹, 5 MPa and H₂/HC_{outlet}: 400. Experiments were carried out at constant oxygen content (0.5 wt %) with 2-propanol, cyclopentanone, anisole, guaiacol, propanoic acid and ethyldecanoate, with the objective to cover a wide range of oxygenated functions. The impact of these oxygenated compounds on the HDS conversion is illustrated in Figure 18. No inhibiting effect on the HDS conversion was observed for 2-propanol, cyclopentanone, or water coming from their dehydration. Similarly, anisole and guaiacol did not inhibit HDS and were converted through intermediate formation of phenols.

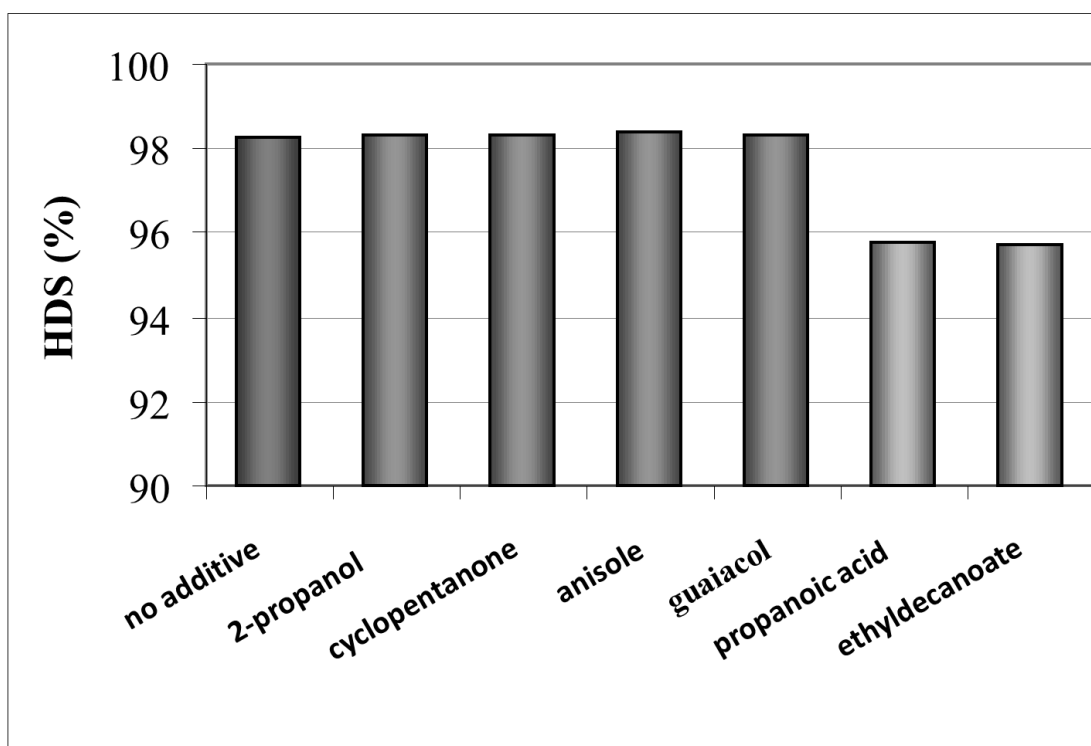


Figure 18. Impact of oxygenated compounds on the HDS conversion of a straight run gas oil at T=330°C, P=5 MPa, 50 cm³ of CoMo/Al₂O₃ sulfide catalyst and LHSV=1.0 h⁻¹ (adapted from ref. [136]).

On the contrary, oxygenated compounds undergoing partial decomposition by decarboxylation, such as propanoic acid and ethyldecanoate, clearly inhibited HDS reactions (Figure 18). By adding propanoic acid or ethyldecanoate to the SRGO, a thermal increment of around 11°C was observed. The thermal increment corresponds to the difference between the actual temperature of the experiment and the calculated temperature that should be applied to the reactor to obtain the same outlet sulphur content as that obtained with the gas oil alone, all other operating conditions being kept constant. This confirms that either these oxygenated compounds or their decomposition products inhibited HDS and HDN reactions, and competed for the same catalytic sites. It was estimated from the analysis of sulphur compounds that the presence of 0.5% oxygen in the form of propanoic acid or ethyldecanoate decreased the HDS reactivity of individual DBT compounds by about 40%.

This study also highlighted the role of CO and /or CO₂ in the co-processing approach. In fact, the conversion of CO on sulfided catalysts has been investigated in the early 80's, the mixture of CO and H₂O being proposed as a reducing gas for hydrotreatment, hydrogen being formed by the WGS reaction, whereas the formation of methane and ethane during the reaction was also evidenced [137]. Therefore, the contribution of WGS and methanation of CO and CO₂ reactions under HDS conditions should be taken into account [138]. In fact, under the ULSD conditions described above, by adding CO the formation of CO₂ was

observed and reciprocally, whereas an excess of methane was also formed (as compared to methane produced during HDS of SRGO), indicating that methanation also occurred.

Therefore, a systematic study of the co-processing of a SRGO was performed in the presence of increasing amounts of CO and CO₂, under similar ULSD conditions, in a fixed bed reactor containing 50 cm³ of catalyst [139]. The CO and CO₂ composition at the reactor outlet always reached the WGS equilibrium, independently of the inlet composition, whereas methanation was under kinetic control. Increasing the amount of CO or CO₂ in the feed-stream was detrimental to HDS, as illustrated in Figure 19. This effect corresponds to a thermal increment between 0 and 22°C in the range of concentrations explored. HDN was affected in a similar way. Moreover, considering the previous experiments performed with propanoic acid and ethyldecanoate (where the decarbonylation/decarboxylation route represents nearly 40%) and the formation of CH₄, CO and CO₂ originating from WGS and methanation reactions, it can be concluded that the inhibition in the presence of the acid and ester compounds is due to the formation of CO and CO₂, and not to the oxygenated reactants themselves. The extent of the inhibition is mainly a function of the total amount of CO + CO₂ whatever the relative distribution of CO, CO₂ or CH₄ formed by WGS or methanation (see Figure 19).

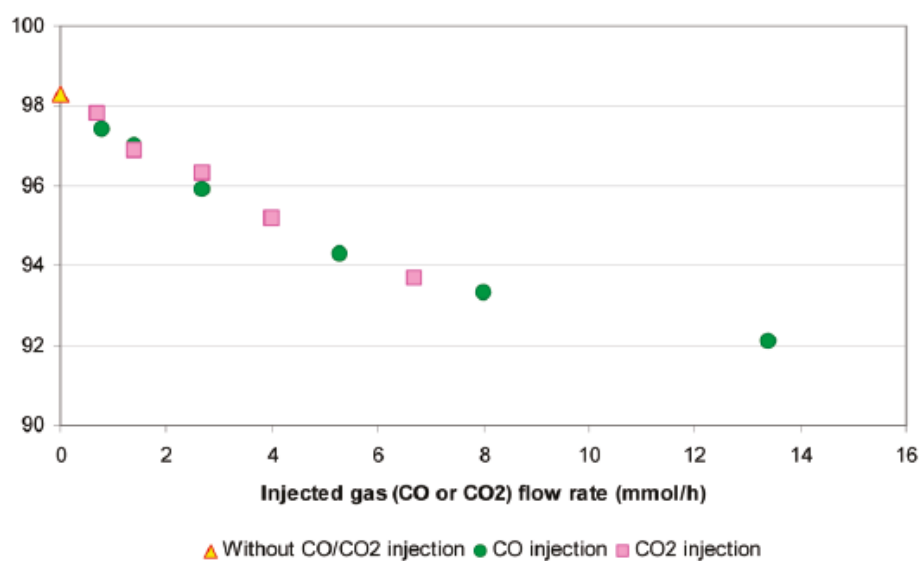


Figure 19. Effect of CO and CO₂ on HDS conversion (T=330 °C, P = 5.0 MPa, LHSV = 1.0 L_{feed}/L_{cata}/h). From ref [139].

HDT co-processing of hydrotreated bio-liquids and SRGO

In the framework of the Biocoup EU project, a series of HDO liquids were co-processed with a SRGO in a continuous flow reactor. These HDO liquids originated from a pyrolysis liquid produced by VTT (Finland) in a 20 kg/h process pilot unit [140] using forest residue as feedstock. After receiving the liquid from VTT, it was kept at -10 °C to avoid aging.

Isopropanol (2 wt. %) was added to the fresh liquid, facilitating the separation of a top layer (10.6 wt.%) containing a large number of extractives. The remaining fraction was used to perform hydroconversions at Twente University to produce HDO liquids [63, 114]. These hydroconversions were performed at 29 MPa in a batch reactor, using a 5 wt.% Ru/C catalyst and reaction temperatures in the range 230-340°C. The conversion lead to various types of hydrotreated bio-liquids, which was separated into an oil fraction (OFWA) and an aqueous fraction (AFWA) by addition of water. Therefore, a series of HDO liquids were provided with various O or water contents and molecular compositions, as illustrated by GPC analysis (see Figure 20).

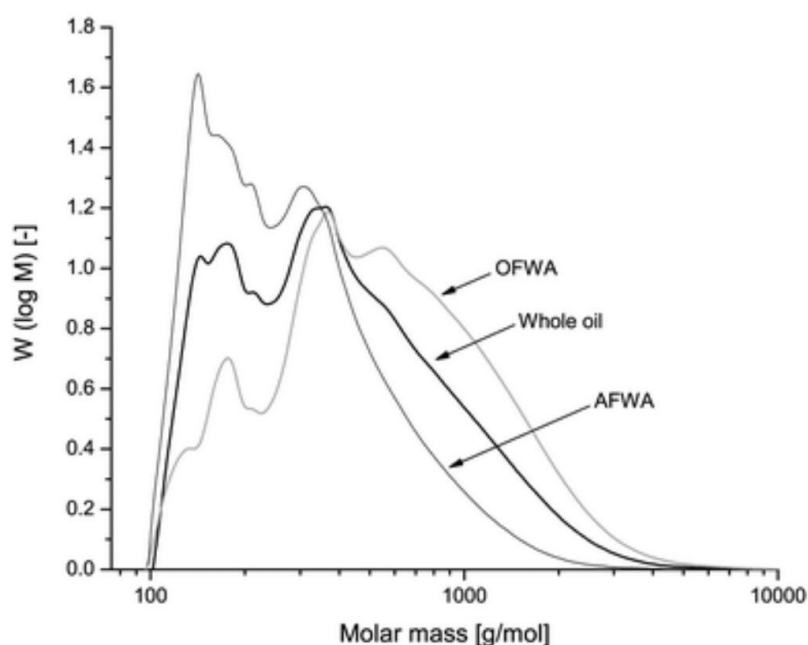


Figure 20. SEC distribution of HDO liquid and its OFWA and AFWA fractions from [113].

The first HDO liquid sample (OFWA fraction) provided by Twente University contained 21 O dry wt.% of and 9 wt.% of water. This HDO liquid was not soluble in the SRGO, therefore several attempts were made to obtain a homogeneous emulsion by adding isopropanol under strong stirring (Ultra turrax disperser operating at 24000 rpm) or with a surfactant (Brij 76) [141]. In both cases, after 2 h of decantation, a viscous phase was observed at the bottom of the tube. As illustrated by SEC analysis, even after HDO treatment, macromolecules were still present in the liquid oil and contributed to this heavy remaining fraction (estimated to ~20 wt.%). This part was removed by decantation and the homogenous mixture of SRGO, isopropanol and soluble bio-liquid was used as the feed for hydrotreatment (100/10/10, respectively, as reference composition).

HDT reaction was performed during 4 days in a continuous flow micro-pilot unit using 1 cm³ of catalyst, starting with SRGO, then SRGO + bio-liquid and back again to SRGO in order to evaluate the catalyst deactivation. As already observed with guaiacol alone, deep hydrodesulfurization conditions were required to prevent HDS performance loss. This was also observed with the mixture reacted at different temperature at a LHSV of 2 h⁻¹ under 4 MPa between 320-360°C. GCxGC-MS allowed to monitor the evolution of phenolic compounds at different reaction temperatures and **showed** the presence of alkyl-substituted phenols families (Figure 21).

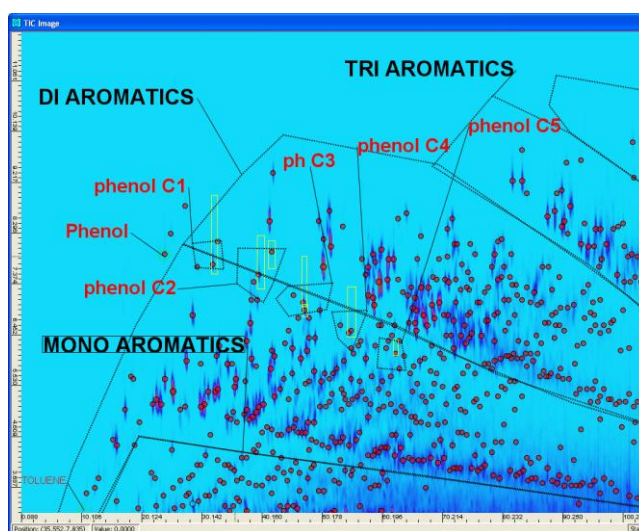


Figure 21. Enhanced view of DBT's area in a GC x GC MS chromatogram (TIC) of the converted SRGO/bio-liquid mixture at 320°C.

The volume of the **GCxGC-MS blobs** corresponding to phenol and substituted phenols provides a semi-quantitative analysis of these molecules during the conversion process. As illustrated in Figure 22 and as observed during guaiacol co-processing, we could notice a clear relationship between HDS inhibition and the presence of phenol type molecules and the requirements **of ULSD operating conditions**. However, contrary to the case of guaiacol where HDS performance was recovered at 360°C, the conversion reached only 95% instead of 99% without **bio-liquid**, indicating another type of inhibition by poisoning. This inhibition was reversible, however, since when only SRGO was fed the performance was fully recovered.

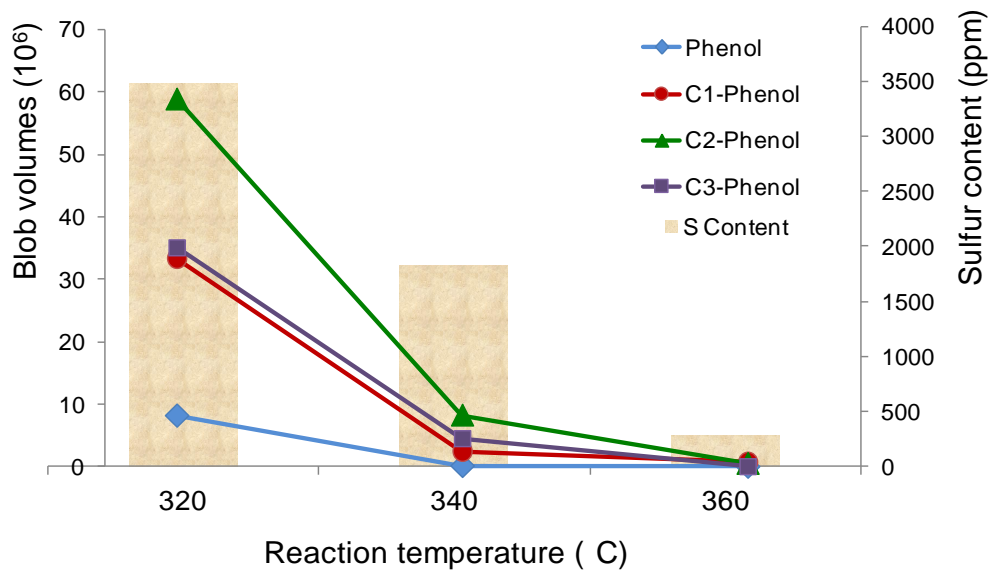


Figure 22. Evolution of HDS performance and transformation of phenol-type molecules at increasing HDS temperatures with a CoMo/Al₂O₃ catalyst.

A catalyst screening was performed at 360°C, and in terms of HDS performances, sulfided CoMo/Al₂O₃ catalyst was found more efficient than NiMo/Al₂O₃ or CoMo/ZrO₂, but the latter catalyst was more selective to remove phenols, as **was already** observed with model molecules [128].

An alternative processing method was also applied. A mixture of the viscous bio-**liquids** in isooctane (30 %) was co-fed with the SRGO, the mixture of the two phases taking place at the entrance of the fixed bed reactor. The feed mixture contained 20 wt.% of pure bio-**liquid**.

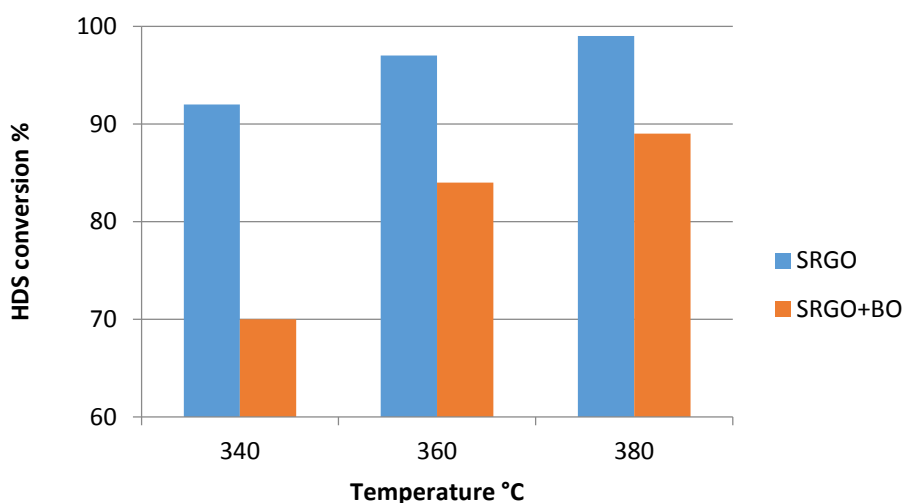


Figure 23. Effect of bio-liquid addition on the conversion of the SRGO on a CoMo/Al₂O₃ catalyst (LHSV 2h⁻¹, 4 MPa).

Compared to the previous introduction method (in which the viscous and non-miscible part of the bio-liquid had been removed), the inhibition was stronger in the presence of the whole bio-liquid (see Figure 23), indicating that the heaviest part of the bio-liquid introduces an extra inhibition of HDS performances. Furthermore, we noticed, as previously observed, that phenol type molecules were normally converted between 340 and 360°C but at 380°C new C₅ and C₆ compounds were observed, which were not found at lower temperature. Therefore, we can assume that the heaviest molecules present in the bio-liquid start to degrade at this temperature, therefore introducing new oxygenates in the media.

The effect of the composition of the HDO-upgraded bio-liquids obtained from [113] was also studied by testing the co-processing of a series of HDO liquids. All HDS co-processing experiments were conducted in a lab-scale unit allowing to co-feed the upgraded liquid with a SRGO. The catalyst used was a commercial sulfided CoMo catalyst, the reactor temperature was 380°C and the LHSV was set to 2 h⁻¹. Both SRGO and upgraded bio-liquids (diluted in isopropanol to reduce the viscosity) were mixed at the reactor inlet.

Depending on the composition of the HDO liquid (see Table 1.), the inhibition under ULSD conditions varied in a wide extent and in some cases phenols were observed in the liquid products. Therefore, the extent of HDS conversion greatly depends on the composition of the HDO liquid, but no direct conclusions can be drawn from the O or water contents. The presence of phenolic compounds was observed with the HDO liquids containing the heaviest molecules (in the whole liquid or OFWA liquid). Initial conversion was almost recovered (98.6 in the worst case) when pure SRGO was fed after SRGO+bio-liquid reactions, showing that the catalyst was rather stable.

Table 1: Composition of various HDO liquids and effect on HDS co-processing under ULSD conditions

HDO liquid (preparation temperature, residence time)	O dry wt.%	H ₂ O wt.%	Sulfur conv. %*
Whole liquid (310°C, 240 min)	19.9	3.5	86**
AFWA (270°C, 240 min)	21.90	7.7	96
AFWA (310°C, 120 min)	18.7	0.8	85

OFWA (310°C, 240 min)	13.6	6.7	97**
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* 99% for SRGO alone, **Presence of phenols

In conclusion, the co-processing of oxygenated molecules originating from bio-liquids with a SRGO in a refinery unit has been investigated using model molecules and mixtures of fast pyrolysis liquid with SRGO in fixed bed continuous flow units (1cm³ 70-50 cm³ of Co(Ni)Mo sulfide catalysts operated at 330-380°C, 50-70 bar, LHSV 1h⁻¹), in order to perform simultaneously HDS and HDO. Since the HDT process is dedicated to hydrodesulfurization and the objective to reach 10 ppm S level in the fuel, the introduction of another feed should not modify this target. From our own experiences, the competition between oxygenated compounds and sulfur ones requires ULSD conditions. Under these conditions, oligomers start to be converted, leading to the appearance of new alkylphenols in competition with the more refractory sulfided compounds. A deep initial deoxygenation is required in the first stage in order to get miscible oil fractions and diminish the competition effect. A further study investigated the co-processing of bio-liquid from *Jatropha Curcas* seed cake with a gas oil and CoMoP/alumina HDT catalysts [142]. At 673 K, when 25% of bio-liquid was introduced in the GO, good quality products were obtained, and under 7.5 MPa of H₂ chars and unprocessable bio-liquid were reduced to 1.5 wt.%. However, the reaction temperature is reaching the limit for this type of catalysts in terms of lifetime and S content was not addressed.

Recently, HDT-Bio-liquid co-processing was investigated with various stream (SRGO, FCC LCO, FCC HCO, LVGO, GO) and identified FCC LCO and LVGO as the most promising candidates for co-processing in HDT units [143].

Co-processing of bio-liquid with vacuum gasoil in a hydrocracking unit.

Co-processing in hydrocracking units is a third alternative offered by conventional refineries. In the framework of 4refinery EC program, IRCELYON is investigating this topic. Up to now, one article reported the use of hydrocracking catalyst (CoMoS on alumina and HZSM-5 mixture) for upgrading different diesel distillate and residual fractions of a bio-liquid demonstrating the ability of the bifunctional catalysts to convert both feed and the recyclability of the catalyst [144], carbon content on the used catalyst was rather small (in the range of 1 wt.%). The interest of hydrocracking is to proceed under harsher conditions than HDT and thus to facilitate the bond breaking of oligomers. It is therefore another option in the co-processing which might be explored and which does not require strong targets such as S content in HDT.

5. Conclusions

This review article summarizes the importance of catalysis and the progress made in the last years on the exploration of the various pathways of valorisation of FP liquids and the contribution of IRCELYON over the last decades to this topic. Fast pyrolysis has been

presented in the literature since the 80's as a promising thermochemical method for producing renewable fuels and chemicals. Pyrolysis itself rapidly reached a potential industrialization but integrated and commercially viable processes were still lacking.

Catalysis has not yet an important role in the current fast pyrolysis process, but new catalytic pyrolysis technologies are evolving. Commercialized solutions based on BFCC or hydropyrolysis are now available and show the need of catalysts. A finishing process involving hydroconversion is required if biofuels are targeted. The impact of the oxygenated compounds on the different reactions and mechanistic aspects are often lacking. Especially the nature and reactivity of macromolecules in pyrolysis liquids still needs further research.

Catalysts are also, however, indispensable in further processing of pyrolysis liquids, such as HDO (either metallic or sulfide catalysts), co-processing (zeolites, sulfides), SR (metals and oxides).

In a near future, the emergence of industrial co-processing methods is expected. Co-processing in hydrotreating units appears to be challenging due to the required ultra-low sulfur levels and the inhibiting effect of oxygenated compounds on the HDS catalysis. Co-processing in hydrocracking units, not yet deeply investigated, seems a better option. Co-processing in FCC units, however, is the most promising and for example, Pyrocell [145] announced recently plans for a fast pyrolysis plant that will supply Preem's Lysekil refinery with pyrolysis liquids. The target of introduction of 10 wt.% of biomass in a FCC process seems to be technically achievable, but will be limited due to the large number of fast pyrolysis units needed. Thus, second generation biofuels produced on one side from lignocellulosic ethanol can now be complemented with thermochemical technologies for diesel or gasoline.

Online SR reforming of pyrolysis vapors remains an interesting option, since it eliminates the issues related to bio-liquids handling and feeding into a SR reactor.

All these developments related to FP wood bio-liquids are now being implemented in the field of waste and more specifically waste polymers conversion. Therefore, the expertise acquired can be used with these new objectives.

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