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RESEARCH ARTICLE OPEN ACCESS

Chemical Commodities via Pyrolysis of Biomass: Phase Equilibria Calculations to Develop Valorization Strategies

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Received: 29 June 2026 | **Revised:** 14 September 2026 | **Accepted:** 12 October 2026

Keywords: Biomasseumwandlung | biomass conversion | erneuerbare Chemikalien | fast pyrolysis | Phasengleichgewichte | phase equilibrium | renewable chemicals | Schnellpyrolyse

ABSTRACT

The production of chemical commodities from biomass via liquefaction, such as fast pyrolysis, is inherently linked to further refining and separation processes. With the latest developments to improve predictive capability of phase equilibria models for fast pyrolysis bio-oil (FPBO), they are now being applied to describe its fundamental behavior in cases that are relevant today. These include condensation of hot pyrolysis gases to recover FPBO and its extraction with water for further fractionation. The results clearly outline the role of condensation for controlling FPBO quality and fractionating products according to boiling points. Various value chains to produce chemical commodities via fast pyrolysis are summarized to evaluate synergetic potential between them.

1 | Introduction

In order to achieve a net-zero CO_2 emission society, it is required to establish an anthropogenic carbon cycle while maintaining today's economic activities. Core of such a carbon cycle will be the recycling of carbon-containing products, which are largely plastics. Carbon losses will be inevitable during recycling and, in consequence, this carbon cycle requires continuous supply of renewable carbon in order to sustain. Both the use of biomass and direct air capture of CO_2 are possibilities to supply such renewable carbon and could be viewed as carbon sourcing and recycling via the atmosphere. In the following, the focus will be on the supply of renewable carbon for bulk chemical commodities from biomass resources.

Biomass as such can be loosely represented as composite material consisting primarily of cellulose, hemicellulose, and lignin polymers. None of these constituents have a value to produce chemical commodities for today's chemical industry apart from niche applications. In consequence, it is required to convert biomass into chemicals that are suitable to serve the needs of chemical industries. The variety of commercially applicable possibilities to achieve this can be divided into two categories: (1) biochemical conversion, which primarily targets carbohydrates as feedstocks and is capable of selectively producing high-value compounds and (2) thermochemical conversion, which is capable of targeting all biomass constituents with the downside of a comparably unspecific compound spectrum produced in a mixture. Due to its scalability and the capability of producing a well-defined synthesis gas containing CO and H_2, gasification of biomass is discussed widely as one key value chain to access a variety of chemical commodities from biomass. This study focusses on fast pyrolysis instead, which is a thermochemical conversion process that aims at producing a liquid, bio-based

Abbreviations: FCC, fluid catalytic cracking; FPBO, fast pyrolysis bio-oil; LLE, liquid–liquid equilibrium; PR EOS, Peng–Robinson equation of state; SOTA, state of the art; VLE, vapor–liquid equilibrium; VLLE, vapor–liquid–liquid equilibrium.

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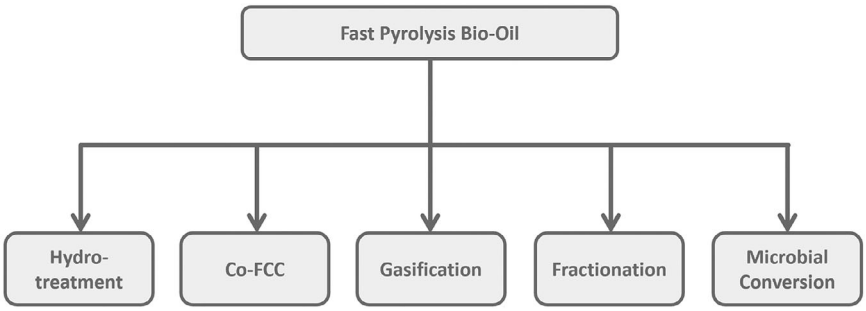


FIGURE 1 | Potential value chains to obtain chemical commodities from fast pyrolysis bio-oil. FCC, fluid catalytic cracking.

commodity. In a modern fast-pyrolysis process, roughly 60% of the energy and carbon content of the biomass is transferred to the liquid, subsequently termed fast pyrolysis bio-oil (FPBO) [1]. FPBO as a commodity itself holds scalable potential to provide chemicals by various means. Fast pyrolysis today is a commercial technology with FPBO being a REACH-registered product that is standardized and marketed to provide alternative fuels for industrial-scale boilers (EN 16900/ASTM 7544; REACH registration with CAS No. 1207435-39-9). The technology development to enable added value uses currently focuses on transportation fuels, specifically aviation and marine fuels. But there are also specific value chains that target the production of dedicated chemicals. The various possibilities are briefly explained in the following, and an overview is presented in Figure 1.

Hydrotreatment of FPBO aims at adjusting the molar H/C and O/C ratios to enable processing of FPBO in existing value chains and end-use applications. Two distinct steps can be distinguished: (1) stabilization to target unsaturated bonds in reactive aldehydes and ketones and (2) hydrodeoxygenation to generally remove oxygen functionalities [2, 3]. Further hydrogenation of aromatic ring structures might be needed depending on the target application. The main driver for FPBO hydrotreatment is the production of liquid transportation fuels aiming at aviation and marine applications. Various cuts are produced after hydrotreatment, which are typically classified into diesel, kerosene, and naphtha fractions according to similarity in boiling point range; however, this does not necessarily mean that they are also chemically similar to fossil-derived counterparts. The low boiling fraction, that is, the "naphtha" range, could potentially be utilized in value chains to produce chemicals if hydrotreatment is realized for the production of fuels.

The coprocessing of FPBO in existing fossil-based refineries is possible and has been tested with various strategies [4]. Conversion of FPBO to cracked products in fluid catalytic cracking (FCC) is low, and the largest part contributes to coking of the catalyst. This can be easily explained with the different constituents of heavy gas oil and FPBO, which can be loosely grouped as hydrocarbon and carbohydrate chemistry, respectively. FPBO conversion can be improved when combined with prior hydrotreatment, for example, stabilization of aldehydes/ketones [5]. The fraction of FPBO that is converted contributes to the product spectrum of the FCC, among which are important chemical commodities. Cofeeding in a commercial FCC unit has been reported [6], that is, it is a relatively advanced FPBO use with comparably little capital investment required.

FPBO has also been demonstrated to be a feasible gasifier feed at MW scale [7, 8]. Biomass liquefaction prior to gasification is an additional effort and will produce a gasifier feed at higher cost than biomass. At the same time, logistics are simplified, and coupling decentralized biomass fast pyrolysis with a central gasifier/synthesis unit allows to make efficient use of economy of scale [9]. Both Fischer–Tropsch and methanol as well as dimethyl ether synthesis are widely discussed in this context, potentially allowing for production of a broad spectrum of fuels and chemicals [10]. This is a very flexible and also robust value chain, given the comparably low quality requirements for FPBO as gasifier feed (e.g., substantial amount of particles in the FPBO are possible [11, 12]). The downside is a comparably high capital investment for the gasification/synthesis unit.

All of above-described value chains can be classified as attempts to forcing the aromatic and highly oxygenated nature of FPBO chemical compounds to fit existing, hydrocarbon-based value chains and uses. A different approach from that is to conceptualize bio-oil as a complex repository of recoverable chemical intermediates, which can be separated, for example, on the basis of solubility, rather than conversion through destructive thermal cracking. Such a value chain based on FPBO fractionation represents a "specialty chemicals" pathway. It is critically important in this context to recognize that an initial separation based on boiling point and vapor pressure inevitably occurs during the condensation of hot pyrolysis gas to recover FPBO prior to any downstream separation process. One comparably advanced (TRL 6–7) FPBO fractionation concept is based on water as solvent [13]. Biomass extractives are removed by a nonpolar organic solvent prior to the actual water extraction step, which results in a "pyrolytic lignin" and an aqueous "pyrolytic sugar" fraction. The lignin fraction functions as a renewable alternative to fossil-derived phenols in industrial resins, used in the production of adhesives and insulation [14]. Importantly, the extraction of the sugar fraction seems to reduce the chemical instability of FPBO [15, 16]. By removing the reactive anhydrous sugars that would otherwise catalyze polymerization into char, stable precursors suitable for sustainable industrial applications are produced. The aqueous "pyrolytic sugar" fraction is concentrated by distillation and has potential for various applications [17, 18].

The availability of "pyrolytic sugars," notably levoglucosan, opens up yet another value chain based on biochemical conversion. In fact, there are well-advanced developments around the application of fast pyrolysis as pretreatment prior to biochemical conversion [19, 20]. It was shown that through passivation of alkali

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and alkaline earth metals, levoglucosan yields of approximately 60 wt% on a cellulose basis can be achieved after fast pyrolysis, which represents the theoretically possible maximum [21]. It was shown that over 85% of anhydrosugars, including almost all levoglucosan, condense at a temperature of 125°C alongside phenolic oligomers [19]. At this temperature, an effective water quench can be applied to selectively condense the heavy organics, whereas retaining water and light oxygenates in the vapor phase. This concept differs fundamentally from using the low-temperature aqueous phase, be it from FPBO extraction or staged condensation [22]. For any of these condensates, the presence of microbial inhibitors is of fundamental importance for subsequent biological conversion. Optimizing staged condensation to strike a balance between the ratio of "nutrients" (fermentable organics) and "inhibitors" (inhibitory compounds) leads to a specific temperature range between 110°C and 120°C for the first stage in order to optimize the second low-temperature stage condensate for microbial conversion [23]. Another approach is the use of hydrophobic polymeric resins to eliminate inhibitory phenolic monomers [24]. The resultant purified stream functions as a versatile feedstock for engineered biocatalysts, such as ethanologenic *Escherichia coli* modified with levoglucosan kinase, facilitating the production of high-value fuels and chemicals.

In conclusion, the combination of these diverse pathways—from the solvent-based stabilization concept to the yield-enhancing passivation/pretreatment techniques—represents a coherent hybrid biorefinery paradigm. In this context, thermochemical processing does not act as a competitor to biochemical conversion but as a facilitator. These integrated platforms yield highly concentrated syrup solutions (surpassing 350 g L^{-1} of bioavailable organics [20]), while overcoming the limitations of long reaction times and dilute effluents from conventional enzymatic saccharification methods. This synergistic approach transforms fast pyrolysis from a purely fuel-generating technology to an advanced platform for biocarbon management and utilization, enabling sustainable industries to leverage the natural complexity of biomass as a strategic advantage.

Phase equilibria calculations are a critical tool to leverage the strategic advances for all of these process chains to chemicals. This fact can be explained in analogy to existing value chains based on fossil crude oil. The initial liquid feedstock is a highly complex mixture of chemical compounds with little value as such. This feedstock requires refining to obtain the broad range of fuels and chemical commodities we are using today. It is impossible to understand the development of modern refineries without the parallel development of phase equilibria models. Although these observations also hold true for FPBO, there is one decisive difference: The quality of the initial feedstock (i.e., FPBO) is governed both biomass source, process conditions during liquefaction, and also the choice of the condensation setup to recover FPBO, which in turn is also based on phase equilibria calculations. Despite the existence of reliable models to calculate phase equilibria, there are specific challenges related to FPBO [25]. Many of these have been addressed in previous work [26–31], allowing for phase equilibria calculations that are suitable to assess the fundamental behavior of FPBO in vapor–liquid (VLE) and liquid–liquid equilibrium (LLE). This information can now be used to assess condensation and subsequent fraction strategies in conjunction with the various possible value chains.

The objective of this study is the assessment of existing valorization strategies for FPBO to produce chemical commodities. Newly developed phase equilibria models are utilized for a fundamental perspective on phase change behavior of FPBO during recovery (i.e., condensation) and downstream liquid–liquid extraction, which represent the two main quality control measures applied today.

2 | Methodology

The phase behavior of fast-pyrolysis products was predicted using a sequential thermodynamic framework integrating independent p–T flash calculations, liquid-phase stability analysis, LLE, and vapor–liquid–liquid equilibrium (VLLE) calculations. Independent p–T flash calculations were performed at specified temperatures and atmospheric pressure following the formulation of Michelsen et al. [32, 33]. The liquid phase was described using the Bio-UNIFAC activity-coefficient model [29], whereas vapor-phase nonideality was represented by the Peng–Robinson equation of state (PR EOS). The PR EOS was employed to provide a thermodynamically consistent evaluation of vapor-phase fugacity coefficients, although deviations from ideal-gas behavior are expected to be modest under the pressure conditions considered in this study [34]. The condensed liquid predicted by the p–T flash calculations was subsequently subjected to liquid-phase stability analysis using the UNIFAC-DMD model [35–40]. Whenever the condensate was found to be unstable as a single homogeneous phase, isothermal LLE calculations were carried out to determine the equilibrium compositions of the aqueous and organic-rich phases. Consequently, systems exhibiting a single stable liquid phase were classified as VLE, whereas systems undergoing spontaneous phase splitting were classified as VLLE.

For the temperatures at which LLE phase separation was predicted, VLLE was evaluated using an activity coefficient-fugacity formulation. Liquid-phase nonideality was represented by activity coefficients calculated with the UNIFAC-DMD model, whereas vapor-phase nonideality was described by fugacity coefficients obtained from the PR EOS. Critical properties, acentric factors, Antoine parameters, and other pure-component thermophysical properties required by the thermodynamic models were derived the same as in a previous study [41]. All thermodynamic calculations were implemented in MATLAB R2024b.

The surrogate mixture used to represent the hot pyrolysis gas that leaves the pyrolysis reactor and enters the condensation setup is detailed in Table 1. The composition is based on the experimental values of wheat straw fast pyrolysis with two-stage condensation down to 20°C [27]. Uncondensed gases were simplified as mixture of CO/CO_2 and added according to experimental values [42, 43]. The compounds are chosen to (1) cover the boiling point range of FPBO, (2) represent characteristic functional groups observed in FPBO, (3) account for major specific compounds contained in FPBO, and (4) focus on compounds with available thermophysical data to compute the activity coefficient model. The choice of the surrogate molecule biphenoltriol to represent oligomers with high boiling points is based on results from ongoing research [26, 44]. An external quench medium and/or solvent for extraction was added for some of the calculations. In this case, the ratio of additional substance to the total amount

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TABLE 1 | Surrogate mixture for fast pyrolysis bio-oil (FPBO) used in the phase equilibrium calculations.

Component	Mass fraction (g g^{-1} vapor)	Normal boiling point (°C)	Ref	Assigned compound class
Water	0.309	100	[45]	n/a
Acetic acid	0.067	118	[41]	Acids
Propionic acid	0.030	141	[45]	Acids
Ethylene glycol	0.004	198	[45]	n/a
Glycolaldehyde	0.031	150	[41]	Aldehydes
Acetol	0.045	146	[41]	Aldehydes
Furfural	0.009	162	[41]	Aldehydes
Phenol	0.002	182	[45]	Phenols
Guaiacol	0.020	206	[41]	Phenols
Syringol	0.020	261	[45]	Phenols
Levoglucosan	0.032	374	[41]	n/a
3,4,4-Biphenoltriol	0.219	496	[41]	n/a
CO	0.068	–191	[45]	n/a
CO_2	0.146	n/a		n/a

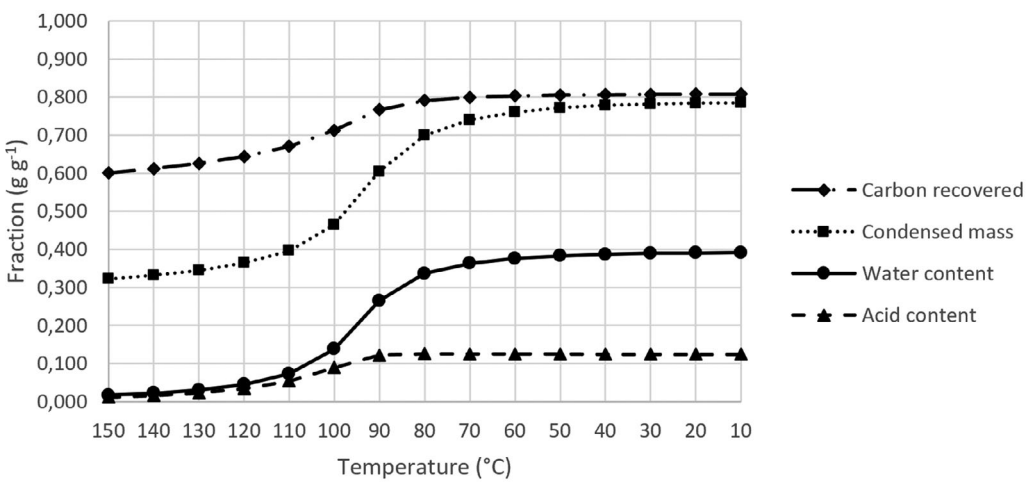


FIGURE 2 | Selected quality characteristics of recovered condensate as function of condensation temperature.

of original material (pyrolysis gas or condensate) was used as parameter. Although ethylene glycol is part of the surrogate mixture and hence included in all calculations, it was not included in the evaluation due to its low mass fraction and little relevance to the investigation.

3 | Results and Discussion

3.1 | Compositional Changes of Pyrolysis Oil Fraction With Various Fractionation Strategies

Condensation of FPBO can be described in two characteristic steps (see Figure 2). As expected, the recovered condensate is dominated by the heavy fraction above 100°C, primarily the surrogate chosen for the unknown oligomer fraction and levoglucosan, but also the majority of phenols and aldehydes. There is also a small fraction of water and acetic acid predicted to condense up to 150°C. The second characteristic step begins just above 100°C with condensation of primarily water and acetic acid. In this stage, the recovered condensate mass fraction increases from around 40% to 70% in a relatively narrow temperature range of 30 K. The carbon recovered only increases by about 10% points in the same temperature range.

The condensation profiles of selected compounds and compound classes are illustrated in Figure 3. Levoglucosan has a constant declining trend with lower condensation temperatures due to dilution effects of lighter species that condense overproportionally. At temperatures above 100–120°C, phenols and aldehydes dominate condensation, that is, their concentration in the pyrolysis condensate increase. With acetic acid and water condensation, this trend is reversed, and all other investigated compounds get diluted. These results show an interesting window for FPBO

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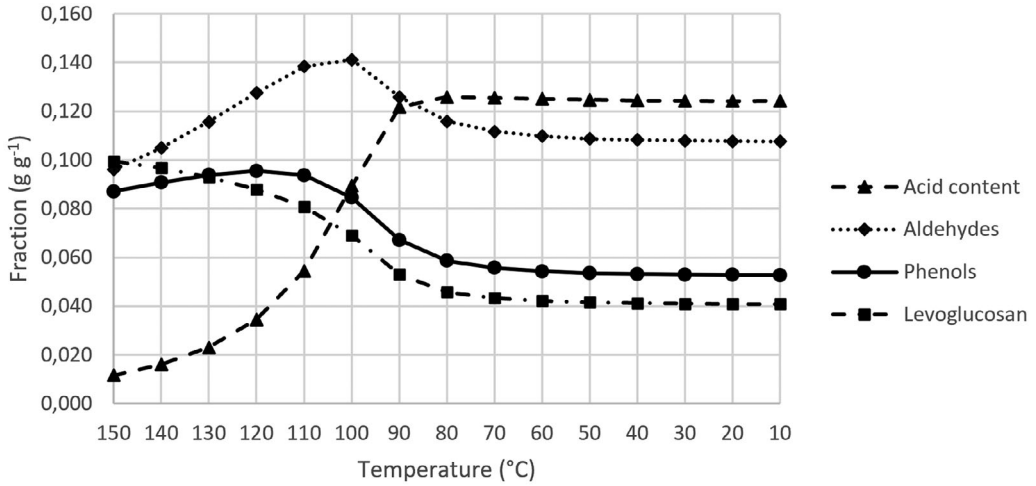


FIGURE 3 | Development of compound (class) concentration in the recovered condensate as function of condensation temperature.

TABLE 2 | Mean values of compound (classes) observed after liquid–liquid phase separation of the fast pyrolysis condensate.

Component	Mass fraction organic rich phase (g g^{-1})	Mass fraction aqueous phase (g g^{-1})
Water	0.23	0.66
Acid content	0.09	0.14
Aldehydes	0.13	0.06
Phenols	0.07	0.01
Levoglucosan	0.06	0.01
3,4,4-Biphenoltriol	0.41	0.07

quality optimization between condensation temperatures of 120–80°C, simultaneously affecting several indicators, such as higher heating value of the condensate, process efficiency (i.e., carbon recovery), viscosity of the condensate (i.e., water/volatiles content), and total acid number of the condensate (i.e., acid content).

Moreover, in this specific setup (wheat straw fast pyrolysis) liquid-phase separation is predicted to occur from 90°C and below. This phenomenon is also reported from experimental studies and related to the feedstock [46]. The model successfully predicts this phase separation and, compared to experimental observations, phase separation is even predicted at similar condensation temperatures of 80–90°C for this specific type of ash-rich feedstock. Results reported elsewhere indicate that phase separation of the condensate is typically not observed at condensation temperatures down to 60°C when feedstocks with low ash content are pyrolyzed [47]. Phase separation of the condensate is considered an undesired phenomenon in most practical applications. The model predicts an organic-rich liquid phase with a surprisingly stable contribution of around 50% of the feed stream mass. Its water and acetic acid content are 23% and 9%, respectively (see Table 2). This liquid phase thus shows a distinctively different characteristic as compared to the condensate recovered at 100°C, however, at a comparable carbon recovery. The amount of the aqueous liquid phase increases steadily at lower condensation temperatures also with a relatively stable water and acetic acid content, that is, these two compounds condense proportionally to other light oxygenates present in the gas phase. It is interesting to observe that also other compounds show a relatively stable concentration in the two liquid phases between condensation temperatures of 90–10°C. This observation leads to the decision to report their mean values in Table 2. All organic compounds except for the acids are predicted with a distribution constant >1.

It is noted at this point that the terms organic-rich and aqueous phase might be somewhat misleading because the molar concentration of water is predicted to be almost 70% due to the difference in molecular weight between water and biphenoltriol. This is not much lower than in the aqueous phase (almost 90%). So, in fact, both phases could rather be viewed as aqueous phases, one of them containing the majority of organic compounds. This is generally in line with experimental results reported elsewhere, in that both water and the pyrolytic lignin are present in significant fractions in both the aqueous and organic-rich phases [48]. Apart from that, there is a puzzling prediction of levoglucosan preferring the organic-rich liquid phase. This is not observed in experiments [49] and requires further investigation to improve the predictive quality of the model.

The adjustment of condensation temperature clearly outlines possibilities to control quality parameters of FPBO to a certain extent, despite obvious trade-offs between various parameters. The results also outline possibilities for a fractionation of FPBO along the boiling points of individual compounds. The multicomponent nature of FPBO will still require extensive effort to achieve relatively pure compounds, but especially water and acetic acid could be potentially reduced in the recovered FPBO with comparably little loss in carbon efficiency. Two-stage condensation offers the opportunity to recover light oxygenates with a separate aqueous phase, but there are no established value chains for this condensate yet.

Another approach to fractionate FPBO along functional groups is by liquid–liquid extraction, and especially water extraction, is one straightforward approach [48]. The formation of a second aqueous phase below condensation temperatures of 80°C could

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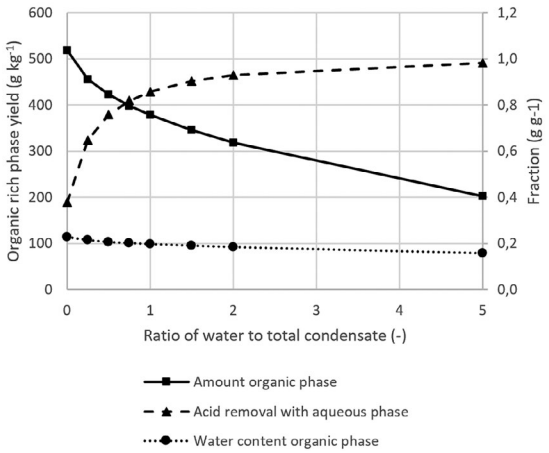


FIGURE 4 | Development of organic phase recovery and its characteristics over the amount of water added to the condensate.

be viewed as liquid–liquid water extraction even though no water is added to the system. Adding more water to the condensate will generally lead to a lower amount of organic-rich phase that can be recovered (see Figure 4), and eventually even a single-phase aqueous condensate is predicted at ratio of 10 and above. Due to a concentration of more hydrophobic compounds in the organic-rich phase, its equilibrium water content decreases. Interestingly, acetic acid can be effectively removed by adding even small amounts of water. It is also obvious that there will be a clear trade-off for various parameters in any case.

It is always desirable to minimize the addition of feeds by utilizing products and side-streams within the process as much as possible. On the basis of this logic, it is state of the art in commercial fast-pyrolysis processes to recirculate the condensed FPBO and use it as quench medium for hot pyrolysis gas after re-cooling. This will lead to consecutive reactions with prolonged residence times at comparably high temperatures [50] and is also likely to affect phase equilibria upon condensation.

In the case that a staged condensation strategy is applied in fast-pyrolysis processes, another aqueous condensate is recovered that could also be used for quenching. This would lead to an excessive amount of water present in the condenser at condensation temperatures below 100°C, that is, only the sensible heat of the quench medium can be utilized. Phase equilibria calculations would predict a single, aqueous condensate under these conditions (i.e., ratio of aqueous condensate to pyrolysis gas of 10 or even higher), which is certainly not feasible as technical solution. The situation changes if the latent heat of vaporization can be utilized at condensation temperatures larger than 100°C, which would reduce the required ratio of quench medium to pyrolysis gas to below 1. In the calculated case of a condensation temperature of 120°C and a ratio of 0.75 (aqueous condensate to pyrolysis gas), the results show the tendency of an improved organic liquid yield. However, it should be noted that examples of FPBO recovered at such high temperatures are being developed but have not reached commercial maturity yet [19].

The aqueous condensate could also be theoretically utilized for the extraction of FPBO in order to avoid the addition of an extraction medium. Due to the presence of extractives in the aqueous phase, performance could be generally rated as slightly inferior to extraction with pure water (see results in Supporting Information). These initial results do not even consider enrichment during recirculation, and more detailed investigations are required for specific cases where the possible/required rate of recirculation can be quantified.

3.2 | The Connection of Fractionation Strategies and Value Chains

The majority of the possible value chains are designed to utilize the whole FPBO (see Figure 5). This is a logic development to improve the carbon to product efficiency and avoid leftover by-products that might represent a waste stream in the worst case. However, it should be noted that the term "whole FPBO" is somewhat unclear because the amount, quality, and composition of FPBO depend on the chosen condensation temperature as shown in above-presented phase equilibria calculations. This temperature sets a clear distinction between condensate (i.e., FPBO) and uncondensed compounds (i.e., pyrolysis gas). Various stakeholders in the field apply different condensation temperatures, which are typically between 60°C and 120°C. As noted above, it is also possible to apply staged condensation which further complicates a clear definition of FPBO. The FPBO, which is REACH registered, shows characteristics that are commonly observed when condensation temperatures between 60°C and 80°C are applied after fast pyrolysis of relatively clean wood. The outlined value chains in Figure 5 exclude each other as they rely on using the whole FPBO, that is, for a given FPBO, these value chains cannot be combined to create synergies. There are

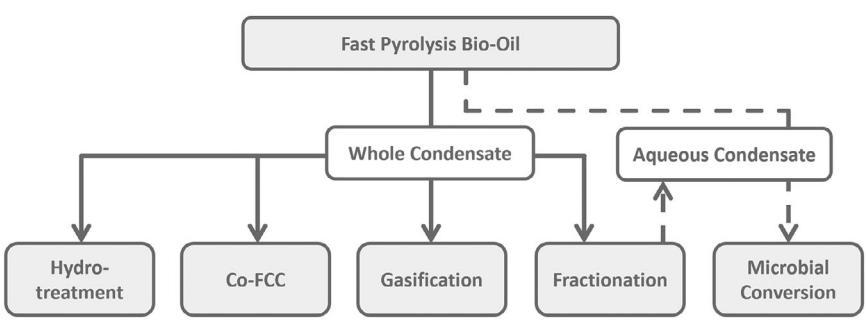


FIGURE 5 | Specific fractions that are utilized for the potential value chains to obtain chemical commodities from fast pyrolysis bio-oil. FCC, fluid catalytic cracking.

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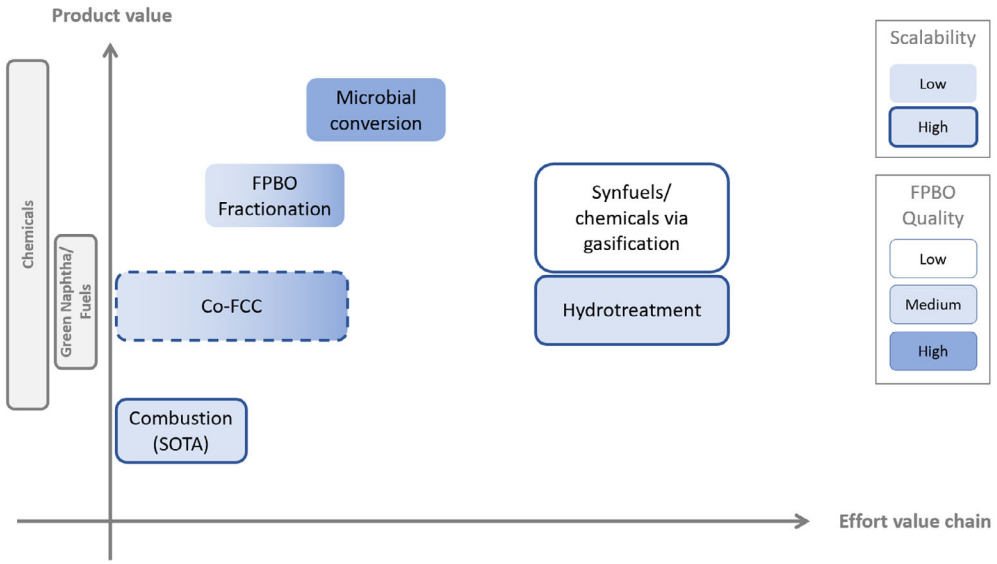


FIGURE 6 | Qualitative arrangement of achievable product values, scalability, and required FPBO quality over the effort of the value chain from FPBO to end product. FCC, fluid catalytic cracking; FPBO, fast pyrolysis bio-oil; SOTA, state of the art.

two exceptions to this observation: fractionation to added-value chemicals and microbial conversion.

Fractionation for the production of chemicals targets relatively specific markets and are subject to sensitive markets, consequently. Even though it targets utilization of the whole FPBO condensate, it remains unlikely that all of the produced fractions retain a high value after commercialization due to a potential imbalance of relatively fixed product shares and market volumes. This opens the opportunity (or need) to valorize fractions of lower value, that is, due to over-saturation of small market segments. One possible strategy for these fractions could be to (additionally) target value chains with larger volumes, such as hydrotreatment to fuels, co-feeding in existing FCCs, and gasification. Specifically, the latter value chain is highly suitable to account for additional liquid fractions that represent by-products from FPBO fractionation due to its robustness. It is even likely that the production of purified compounds from FPBO fractionation becomes more viable once gasification of FPBO is established because the clear value by-products from purification will have in such a case.

One very different product of fast pyrolysis is utilized in the biochemical value chain because microbes primarily process organics in aqueous media. In commercial fast-pyrolysis installations, aqueous condensates are not recovered and instead added to process internal combustion without condensation. This means that commercial pyrolysis processes need to be adapted in order to recover an aqueous condensate, for example, by adding a second condensation step at lower temperatures. Although such setups have been developed up to TRL 6, commercialization is still pending and the availability of an aqueous condensate is a hypothetical case, consequently. This also means that aqueous condensate can be produced by fast pyrolysis without affecting recovery and utilization of the main product FPBO. It follows that microbial conversion is a synergizing value chain approach to all other possibilities outlined. It is noted that one fractionation approach for the production of chemicals is extraction of FPBO with water. This naturally yields an aqueous extract and depending on the achievable product values, this aqueous extract could alternatively—or additionally—be valorized in a biochemical value chain (see Figure 5).

The potential product value and efforts of the required value chain are also two decisive considerations for FPBO valorization. A qualitative arrangement of these two indicators for the various FPBO value chains is summarized in Figure 6. It is clearly visible that a higher effort over the value chain does not necessarily lead to an improvement in product value. Specifically, microbial conversion and fractionation for the production of chemicals stand out as examples with high ratio of product value over value chain effort; however, they also represent value chains with limited scalability (either in terms of technology or product market size). Co-FCC is a special case as it comes with a very low entrance barrier due to the fact that existing infrastructure is utilized. At the same time, it is to be expected that this infrastructure will experience severe changes in case the use of fossil crude oil is phased out. Moreover, carbon conversion efficiency from FPBO to end products is comparably low because the applied catalysts are optimized for fossil hydrocarbon feedstocks. The effort of hydrotreatment and synfuels via gasification is rated with a similar effort over the value chain. Due to the flexibility of fuel synthesis, higher value products in the domain of (bulk) chemicals are possible as compared to the rather unspecific nature of current hydrotreatment approaches.

4 | Conclusions

Efficient valorization of FPBO requires reliable predictions of its distribution during various phase equilibria. This is of fundamental importance for both downstream separation processes and the recovery of FPBO itself, which involves choosing an appropriate condensation temperature (depending on feedstock, pyrolysis conditions, and intended end-use). The development of phase equilibria models that address specific challenges of FPBO

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allows fundamental description of FPBO behavior under various, application-oriented conditions.

Condensation of FPBO always represents a first fractionation step, even if a single condensation stage is chosen. It inevitably separates the main product FPBO from the uncondensed fraction, which still contains a variety of volatile organic compounds. Condensation of pyrolysis gas can be characterized by two distinct phases—the condensation of primarily phenolic oligomers together with levoglucosan, phenols, and aldehydes at temperatures above 120°C and a subsequent condensation of primarily water together with acetic acid between 70°C and 100°C. This means that both water content and acidity of FPBO can be influenced with a careful choice of condensation temperature. It was also shown that water extraction of FPBO is an effective measure to reduce its acidity at the cost of additional carbon loss with the aqueous extract. One decisive feature is the transfer of polar molecules with high boiling point, such as levoglucosan, to the aqueous phase, which opens up additional value chains.

Internal use of fast-pyrolysis products for both condensation and liquid–liquid extraction has been investigated. Recirculation of the aqueous phase for FPBO extraction reduces the efficiency of this step, but might be a worthwhile consideration for specific cases.

An evaluation of the various value chains from FPBO to chemical commodities reveals strong synergies between biochemical use of pyrolysis condensate and all other potential value chains. However, the presence of various inhibitory compounds is a challenge that still requires attention in order to make this a viable alternative.

Acknowledgments

This work has been funded by the German Federal Ministry for Economic Affairs and Energy (project number 03EN2145B).

Open access funding enabled and organized by Projekt DEAL.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

The detailed results of the VLE and VLLE

calculations are provided as Excel Sheet.

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