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Influence of selected quench media used for direct contact condensation on yield and composition of fast pyrolysis bio-oils aided by thermodynamic phase equilibria modelling

George Kofi Parku *, Axel Funke, Nicolaus Dahmen

Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

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ABSTRACT

Direct contact (quenching) condensation of fast pyrolysis vapours into fast pyrolysis bio-oils (FPBOs) is associated with the advantages of high efficiency, improved thermal performance and significant reduction in process cost. However, choosing a suitable quench media (QM) for the process remains a challenge and it has been a subject of ongoing investigations in the quest to optimising the recovery of FPBOs. In this study, the influence of four QM that include water, Isopar-V, ethanol and ethylene glycol on the product yield and composition of FPBOs were evaluated. Different ratios (0.5 and 2.0) of the respective QM to hot pyrolysis volatiles (m_q/m_v), which define the quenching temperature and extent of cooling were probed. Ethanol recovered the highest yield of the organic-rich condensate (ORC) fraction of the FPBOs, most particularly at the m_q/m_v ratio of 2.0, which produced 50 wt% more ORC than ethylene glycol and 75 wt% more than water and Isopar-V. Ethylene glycol proved to be the most efficient QM for the recovery of carboxylic acids, ketones and phenolic compounds in the ORC. Isopar-V largely demonstrated immiscibility with the ORC, however, some slight interactions with the ORC product were evident. For the water quench, owing to its significant interactions with the ORC, nearly all water-soluble compounds, particularly sugars ended up in this quench following condensation, making it valuable for the recovery of sugars directly during quenching. Phase equilibria model prediction of the quenching condensation process with the modified UNIFAC Dortmund (UNIFAC-DMD) thermodynamic model showed huge prospects specifically in predicting product yields and the chemical composition of the ORC. Nevertheless, the limitations of this model became apparent in scenarios that include predicting low concentrations of organics in water, association and hydrogen bonding interactions as well as uncertainties associated with pure component vapour pressure data of some compounds. Regardless, the study proves to be a significant addition towards optimising the selective recovery of valuable chemicals from FPBOs during direct contact condensation.

1. Introduction

Biomass conversion into energy, fuels and useful chemicals has gained strong attention owing to the conscious comprehensive effort in mitigating global warming effects by switching to the use of bio-based instead of fossil feedstocks [1–3]. Fast pyrolysis converts lignocellulosic biomass into fast pyrolysis bio-oil (FPBO) alongside char and non-condensable gases. FPBO is a standardized fuel for industrial scale boilers and can also serve as a precursor for the production of transportation fuels and chemicals/materials [4–6]. Pyrolytic products leaving the pyrolysis reactor are complex composition of condensable vapours, non-condensable gases, liquid aerosols and solid particulate matter. Hence, condensation of pyrolysis volatiles generated following fast pyrolysis plays a key role in optimising the yield and composition of recovered FPBOs [1,2,7–10]. The most commonly used condensation schemes for pyrolysis systems are direct contact heat exchangers (spray/quench columns) and indirect contact heat exchangers (shell and tube) [9]. Indirect contact heat exchangers have seen numerous applications mostly for laboratory bench-scale systems [11,12]. They are associated with comparatively low cooling rates and difficulties with the removal of highly viscous FPBOs especially at lower temperatures [11]. They are also typically associated with blockages of pipelines and the heat exchanger as well as fouling and corrosion, which normally arise from the deposit accumulation of lignin-derived, high molecular weight components [7,13–15].

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* Corresponding author.
E-mail address: george.parku@kit.edu (G.K. Parku).

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Nomenclature

Abbreviations

AARD	Average absolute relative deviation
AC	Aqueous condensate
ARD	Absolute relative deviation
FPBO	Fast pyrolysis bio-oil
NCG	Non-condensable gases
ORC	Organic-rich condensate
PDU	Process Development Unit
QM	Quench media
UNIFAC-DMD	modified UNIFAC Dortmund
VLE	Vapour liquid equilibrium

Symbol(s)

(m_q/m_v)	Mass flowrate ratio of the quench to the hot pyrolysis volatiles

The use of direct contact heat exchangers for the condensation of FPBOs have been reported to circumvent the above-mentioned limitations associated with the indirect contact heat exchangers and facilitate greater contact area between cooling fluids and pyrolysis volatiles [14,16]. This consequently enhances the rapid cooling of the pyrolysis volatiles, minimising undesirable secondary cracking reactions, which are known to favour the production of non-condensable gases at the expense of FPBOs [2,7,13,15,17–19]. As a result of their improved thermal performance, direct contact heat exchangers also usually require up to 60% less cooling fluids than their corresponding indirect counterparts [14]. For these reasons, they contribute to the reduction of their overall process cost, making them more economically viable and the most preferred choice for industrial applications [14,16,17].

Notwithstanding, the use of direct contact heat exchangers are characterised with limitations that include interactions such as mixing, reactions and mass transfer of components between quench media (QM) and FPBO. This consequently affects the yield, stability and composition of recovered FPBO. In effect, potentially high cost of downstream separation and treatment methods are required in order to obtain desired FPBOs [14,16]. To mitigate this, a number of studies employed the use of paraffinic and naphthenic hydrocarbon oils as QM owing to their immiscibility with the recovered organic-rich condensate (ORC) fraction of the FPBO. Westerhof et al. [10] employed one such hydrocarbons, named the Shell Ondina 941 oil as QM in rapidly cooling the hot pyrolysis volatiles generated from fast pyrolysis of pine wood. In another study, the authors employed a similar hydrocarbon liquid (Shell Ondina 917) with slightly different physicochemical properties [1]. Park et al. [13] also employed a hydrocarbon oil (primarily made up of mixtures of paraffinic and naphthenic compounds) as quench for condensing the hot volatiles obtained from the fast pyrolysis of larch sawdust. Palla et al. [7] used octane at −5 °C as direct contact quench for the condensation of hot pyrolysis vapours. The fast pyrolysis technology developed at CanmetENERGY-Ottawa, Canada utilised an isoparaffinic hydrocarbon mixture quench fluid (Isopar-V) for condensing hot pyrolysis volatiles into FPBOs [20–22]. They cited low vapour pressure, thermal stability and its immiscibility with the ORC as the key reasons behind its selection.

Contrary to the use of such high boiling point QM, other studies also employed the use of highly volatile QM such as liquid nitrogen, ethanol and acetone such that they are immediately flashed into vapours upon contact with the hot pyrolysis volatiles and do not end up mixing with the recovered ORC. For instance, Treedet et al. [12] used ethanol as quench for the recovery of bio-oil generated from the fast pyrolysis of some selected herbaceous and agricultural biomass feedstocks. Dalluge et al. [23] developed a novel quench system, which employed liquid nitrogen as quench to rapidly cool hot volatiles generated from the fast pyrolysis of cellulose. In the same study, water was employed as quench on a pilot-scale version of the system, citing water as less expensive especially for commercial applications. Elsewhere, the research group also employed the technique with liquid nitrogen as quench for sugar production, following the fast pyrolysis of acid-infused lignocellulosic biomass [24]. The technology was also employed in another study by Kim et al. [25], who investigated the recovery of resin acids from the fast pyrolysis of pine.

As a common practice for most state-of-the-art large and industrial-scale systems, the produced ORC fraction of the FPBO itself is utilised as quench. In that case, an initial starting quench liquid is required. In commercial units, this typically would be previously produced and stored ORC. There are also cases from R&D units that recirculate the produced ORC to utilise as QM. However, given the nature of their operation, different start up QM are used. One example is utilising ethylene glycol (glycol) as starting quench material, which is readily miscible with the produced FPBO [26–28]. The studies of Chang et al. [2] and Zheng Ji-lu et al. [29,30] also employed acetone and ethanol as starting quench liquid, respectively, citing high volatility as the reason behind the choice of these starting quench materials.

In most of these cases, choice of QM was based on pragmatic considerations (e.g. miscibility/immiscibility with FPBO) and/or process optimization considerations such as QM cost and boiling point. However, complexities of how these commonly employed QM impact the characteristics of FPBOs have not yet been fully established and they remain a subject of ongoing investigation.

Furthermore, modelling the vapour-liquid equilibrium (VLE) of condensation systems permits for the study of separation systems without the time and effort required in performing these studies in real setup cases. In addition, it also helps ascertain key unexplained phenomenon, which are normally encountered during experimental investigations. In a previous study [31], where the optimisation of the composition of the aqueous fraction of FPBO for its application as substrate was investigated during condensation, the use of the modified UNIFAC Dortmund (UNIFAC-DMD) thermodynamic group contribution model further demonstrated how crucial modelling such systems can be albeit not without limitations.

The objective of this study is to test the hypothesis that the choice of QM affects phase equilibria and consequently the chemical composition of recovered FPBOs. Four commonly utilised QM that include Isopar-V, water, ethylene glycol and ethanol are evaluated. VLE modelling of all the direct contact (quenching) condensation scenarios were applied to provide a theoretical basis to understand underlying effects and specific condensation conditions have been applied experimentally to validate theoretic findings.

2. Materials and methods

2.1. Materials

Wheat straw feedstock supplied by Franz Kolb GmbH & Co. KG, Germany (firma-kolb.de) was provided in 300–400 kg bales and further reduced to particle sizes below 5 mm using a shredder (HZR 1300) and a cutting mill (TYP LM 450/1000-S5-2). Both size reduction equipment were supplied and installed by Neue Herbold Maschinen- und Anlagenbau GmbH (Sinsheim, Germany).

Isopar-V was manufactured by Exxon Company, USA and was supplied by LCG Limited, UK. It primarily contains $C_{14} - C_{18}$ isoparaffinic hydrocarbon atoms with boiling point range between 273 and 311 °C. It has an average molecular weight of 197 g/mol and a specific gravity of 0.82 at 15.6 °C.

Demineralised water used for water quenching experiments was supplied by the facilities management of Karlsruhe Institute of Technology (KIT) at ambient temperature and 4 bar pressure.

Ethanol (99.5 vol%), denatured with about 1 vol% methyl ethyl ketone was manufactured by VWR Chemicals BDH, France and was supplied by Häffner GmbH & Co. KG, Asperg, Baden-Württemberg, Germany.

Ethylene glycol was supplied by Brenntag GmbH, Essen, Germany. It has a molecular weight of 62.07 g/mol, boiling point of 197.4 °C and a density of 1.122 g/cm^3 at 20 °C.

2.2. *Fast pyrolysis conversion and the direct contact condensation process*

Fast pyrolysis of wheat straw was conducted on a 10 kg/h fast pyrolysis process development unit (PDU), a scaled-down version of the bioliq® process [26,32]. Detailed operation processes of this unit has been provided elsewhere [28], thus only a brief description of modified operations are provided in this study.

For a much simpler and easy approach to control the condensation process, a bypass condensation system (Fig. 1) with design and operating conditions similar to the conventional condensation system (main quench loop) of the PDU was employed. With this, all the pyrolysis volatiles exiting the hot part of the reactor are channelled through the bypass, first passing a filter to retain solid particles before they come into contact with the quench to recover the ORC. Unlike the main condensation loop, QM is externally supplied continuously throughout the duration of the experiment without recirculation of the QM/ORC product.

Following quenching, the liquid mixture at temperature, T_1 (Fig. 1) proceeds to a heat exchanger, where it is condensed for the subsequent recovery of the ORC. Set temperatures, T_2 (Table 1) for this heat exchanger were selected based on the volatility and boiling point of the QM in question. Volatiles, which could not condense on this stage proceed to an electrostatic precipitator, where aerosols are captured before they proceed to a second heat exchanger operating at 6 °C to recover a water rich aqueous condensate (AC) (Fig. 1). Non-condensable gases are then analysed using an online gas chromatograph before being discarded. During the course of the experiment, entry to the main quench loop is completely closed to ensure that all volatiles are channelled into the bypass. To keep up with the comparatively low volume capacity of the bypass, biomass feed rate was adjusted to within the ranges of 1.5 to 2 kg/h.

The mass flowrate ratio of the quench to the hot pyrolysis volatiles (m_q/m_v) defines the quenching temperature and consequently the extent of cooling of the hot pyrolysis volatiles. Two different m_q/m_v ratios of 0.50 and 2.0 were investigated. Temperature of the pyrolysis volatiles from the hot part of the reactor prior to quenching ranged between 380 and 385 °C and temperatures of the resultant QM/ORC mixture was principally dependent on the properties of the QM in question and its heat of evaporation. These temperatures (T_1) have been presented in Table 2. All experiments on the PDU were conducted in duplicates to ensure repeatability.

Table 1
Set condensation temperatures (T_2) of the ORC condensation stage for all QM investigated (chosen based on the volatility and boiling point of the QM in question).

Quench	Condensation temperature on ORC recovery stage (°C)
Isopar-V	80
Water	95
Ethylene glycol	80
Ethanol	40

2.3. *Condensate characterisation*

The moisture content of all condensates was determined by volumetric Karl-Fischer-titration. Hydranal methanol was used as solvent and the titration was conducted using Hydranal Composite-V as titrant. An automated titration equipment, Metrohm 841 Titrando/800 Dosino was utilised. All reagents were supplied by Sigma Aldrich.

GC–MS/FID characterisation of all condensates were conducted by the Thünen Institute, Hamburg, Germany. A description of the method employed has been elaborated elsewhere [33]. GC–MS analyses of all condensates have been presented in Tables S7 to S16 of the supplementary information.

Table 2
Temperatures of QM/ORC mixture (T_1) following direct contact with respective QM.

Quench	Temperatures of QM/ORC mixture (°C)	
	m_q/m_v – 0.50	m_q/m_v – 2.0
Isopar-V	179	133
Water	169	86
Ethanol	148	50
Glycol	153	115

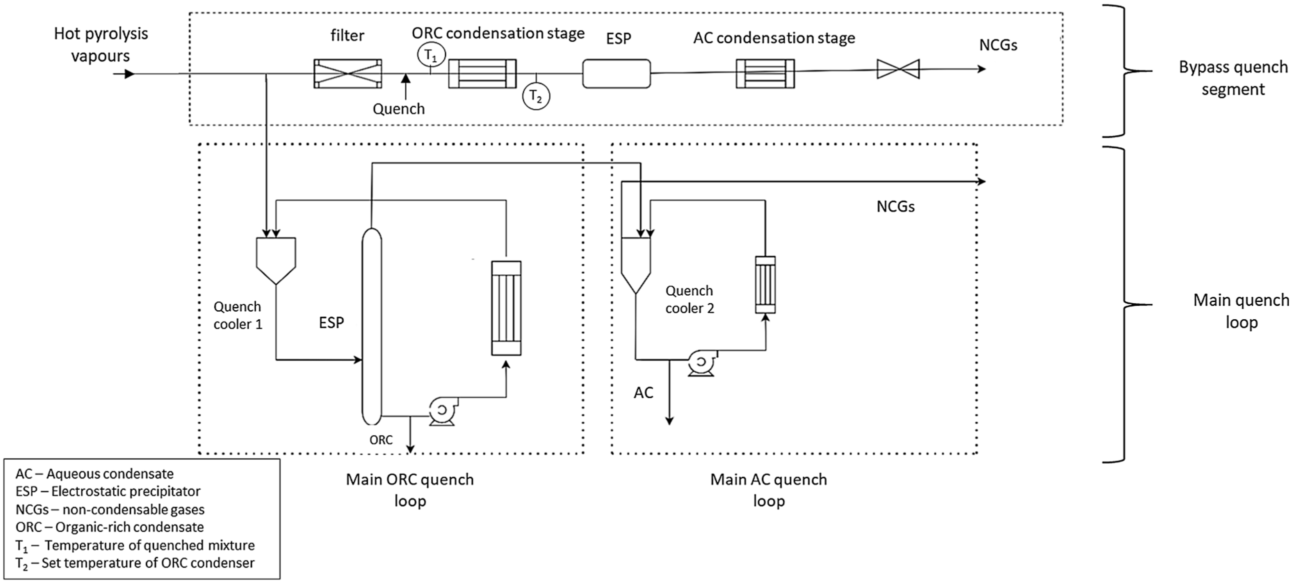

Fig. 1. Schematic representation of the fast pyrolysis process development unit (PDU) demonstrating the main quench and bypass condensation systems.

2.4. ASPEN plus model simulation of condensation system

The phase equilibrium at the given conditions during condensation was simulated in ASPEN Plus® V12 to predict how the variable parameters (QM, flash temperature and m_q/m_v) affect the yield and composition of FPBOs.

A surrogate mixture (Table S1 of supplementary information) that represents the composition of hot pyrolysis volatiles and serves as input to the condensation unit was first developed. The selection of surrogate compounds followed similar procedure as detailed elsewhere [31,34], making use of data determined by the GC–MS analysis of FPBOs, GC characterisation of non-condensable gases and the mass balance of the condensation process from fast pyrolysis experiments of wheat straw.

Following the definition of the surrogate mixture, the ASPEN flowchart simulation was setup as represented in Fig. 2. The quenching of hot volatiles (VAPORS) by the respective QM (QUENCH) was modelled as a mixer (QUENCH1) operating at 1 bar. Thereafter, the QM/ORC mixture (QUEMIX) proceeds to the first condensation stage (K1), which is modelled using the ASPEN flash module. On this stage, the phase equilibrium of the mixture is modelled at the respective temperatures (Table 1) to recover the condensate, which comprises a mixture of the ORC and the spent QM (LIQ). For the cases of Isopar-V and water being immiscible with the ORC, the ORC/QM mixture (LIQ) is subsequently subjected to a further downstream separation modelled as an adiabatic decanter at 1 bar (DECANT). On this stage, the spent QM (TOPS) is separated from the ORC. Virtually no gasses (GASDEC) are generated on this unit.

Volatiles which could not condense on K1 proceed to the second condensation stage (K2), where they are cooled down to 6 °C to recover the AC (modelled using the ASPEN flash module). Non-condensable gases (GASK2) are then expelled. UNIFAC-DMD was employed in estimating the physical properties of all defined components.

Deviations of theoretical model predicted data ($Z_{calc,i}$) from respective experimental data ($Z_{exp,i}$) were quantified using the absolute relative deviation with respect to experimental data (ARD%) and the average absolute relative deviation (AARD%) for N number of data points. These have been defined by Eqs. (1) and (2), respectively.

$$(ARD\%)_i = \left|\frac{Z_{exp,i} - Z_{calc,i}}{Z_{exp,i}}\right| * 100 \tag{1}$$

$$AARD\% = \frac{1}{N}\sum_{i}^{N} ARD_i \tag{2}$$

3. Results and discussions

3.1. Effects of quench media type on yield distribution of FPBOs

Hot pyrolysis volatiles exiting the reactor are first filtered to retain any solid particles before they come into contact with the quench. The quenched mixture then undergoes condensation on the first condensation stage, operating at set temperature conditions (Table 1), which were chosen based on physical properties such as volatility and boiling point of the QM being utilised. Consequently, the ORC is recovered on this stage. It is noteworthy to mention that the varying volatilities and boiling points of the different QM investigated warranted distinct condensation temperatures for efficient recovery of FPBOs, most particularly for ethanol and water. In effect it was not possible to use the same temperature conditions for all QM, which has been noted as a limitation associated with investigating QM with different physical properties on a comparative basis.

Successively, the QM that did not mix with the ORC (Isopar-V and water) were further decanted to separate the recovered ORC from the spent quench. Volatiles which could not be captured on the first condensation stage were cooled on a subsequent stage to recover the AC. On average, a majority spent fraction of about 92 and 99 wt%, respectively of total Isopar-V and glycol originally utilised were recovered together with their corresponding ORCs on the first condensation stage (Table 3). Ethanol, owing to its high volatility and rather low boiling point had spent fractions significantly distributed on both condensation stages, recovering on average about 45 and 30 wt%, respectively. Accordingly, significant fractions of ethanol in the range of 20–25 wt% were lost as vapours together with the non-condensable gases. As it forms a homogenous mixture with the AC, spent water quench recovered on the second condensation stage could hardly be quantified.

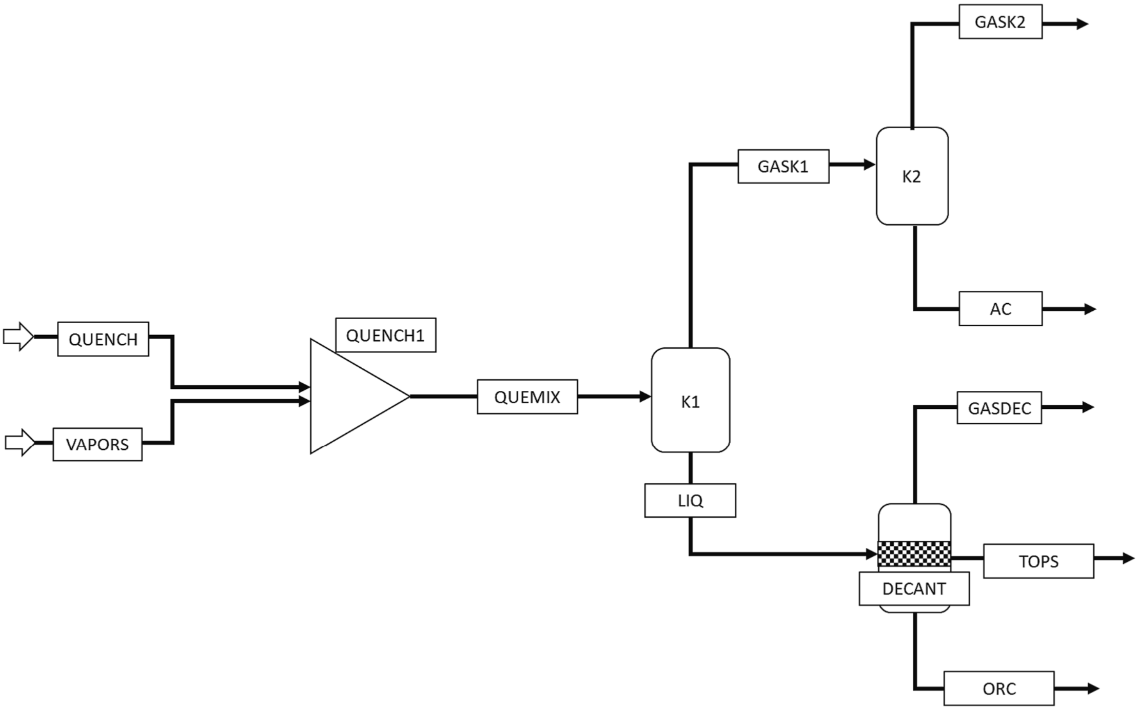

Fig. 2. ASPEN flowchart of the bypass condensation process.

Table 3
Fractions (wt%) of spent QM recovered on both condensation stages.

	m_q/m_v – 2.0		m_q/m_v – 0.5	
Quench	condenser 1	condenser 2	condenser 1	condenser 2
Isopar-V	95.8	0.1	89.0	0.52
Glycol	>99.0	<1	95.0	<1
Ethanol	60.1	18.5	30.3	42.4
Water	81.7	n/a	50.1	n/a

Nonetheless, a little over 80 wt% (m_q/m_v of 2.0) and 50 wt% (m_q/m_v of 0.5) of total water-quench used were recovered on the first condenser stage (Table 3).

The effects of all the investigated quench media (QM) on the product yield distribution of both ORC and AC are depicted in Fig. 3. Yield distribution of all FPBOs have been presented on dry and QM-free basis. The effects were interrogated for two different mass flowrate ratios of QM to pyrolysis volatiles (m_q/m_v = 0.5 and 2.0), which define quenching temperature and the extent of cooling of the hot pyrolysis volatiles. Product yields were calculated with respect to the total amount of pyrolysis volatiles entering the first condensation stage. Thermodynamic phase equilibria model predictions of the condensation effects associated with each QM (Fig. 3b) was also probed and compared with experimental data (Fig. 3a).

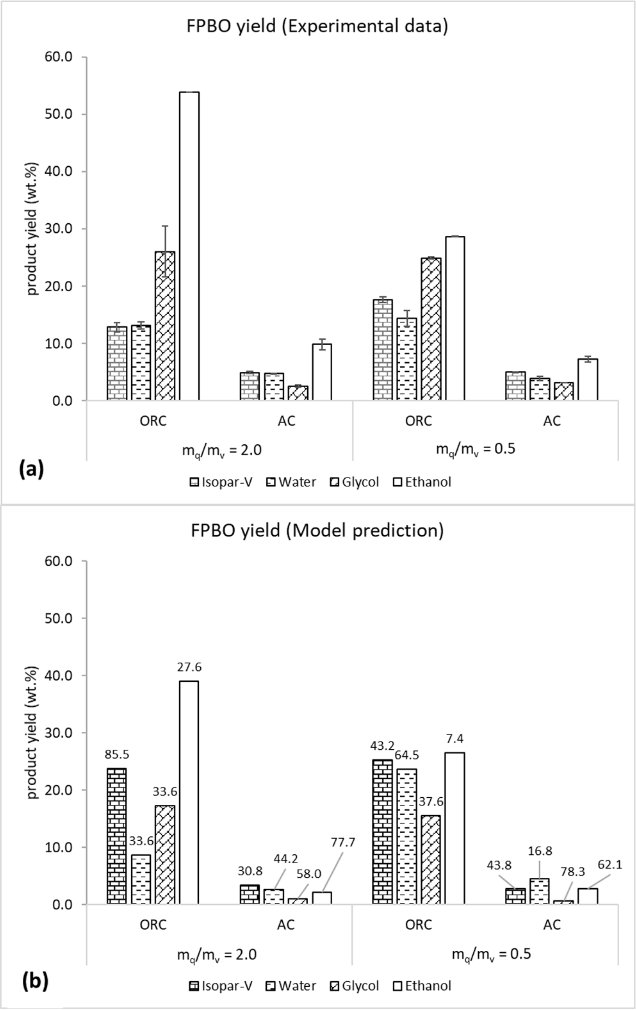

Fig. 3. Effects of all investigated QM on yield of FPBOs (ORC and AC): (a) experimental data and (b) model predicted data showing individual absolute relative deviations (ARDs) with respect to experimental data. Yields have been reported on dry and QM-free basis.

3.1.1. *Experimental investigations*

At m_q/m_v of 2.0, ethanol yielded the highest fraction of ORC, recovering about 54 wt% of pyrolysis volatiles as ORC. This was followed by ethylene glycol, which yielded about 26 wt% of volatiles as ORC. Water and Isopar-V recorded the least amounts of ORC, recovering only about 13 wt% each (Fig. 3a). Similar trends were observed at m_q/m_v of 0.5, except that the yield of ORC recovered employing ethanol as quench for this instance significantly decreased to about 29 wt%. This suggests that higher ethanol-quench to volatiles ratio increased interactions (as observed and discussed in section 3.2.2) between ethanol and dominant compounds such as carboxylic acids and ketones present in the pyrolysis volatiles, which led to their increased condensation in the ORC. Ethanol at this condition of m_q/m_v also recorded a significantly lower temperature of QM/ORC mixture (50 °C) (Table 2), a cold enough temperature to suppress any chances of secondary cracking reactions from occurring and hence the recovery of comparatively higher yield of the ORC.

It was subsequently evidenced that those QM, which formed a mixed product with the ORC (ethanol and glycol) recorded higher ORC yields than the immiscible ones (Isopar-V and water). This was corroborated to the loss of organic compounds from the ORC, arising due to the mass transfer of molecules between the ORC and the immiscible QM. Although, Isopar-V has demonstrated promising immiscibility with the ORC, this effect was not completely ruled out for this QM due to its pigmentation following quenching. This was also ascertained in a similar study conducted by Bronson et al. [22]. Their study reported the incidence of emulsification of Isopar-V in ORC as a consequence of mass transfer between both fluids, which was very much conspicuous for ash-rich biomass feedstocks (wheat straw being a typical example).

For all QM and at both m_q/m_v ratios, the fractions of pyrolysis volatiles that were recovered in the second condensation stage in the form of AC were not more than 10 wt% (Fig. 3a). Ethanol as quench generated the highest AC fraction at both m_q/m_v ratios, producing nearly twice as much AC as the other investigated QM, whose AC yield were only on average about 4 wt%.

3.1.2. *Model prediction*

Average absolute relative deviations (AARDs) of model predicted data with respect to experimental data for all QM (Fig. 3b) for the yields of ORCs ranged between 38.2% (m_q/m_v of 0.5) to 45.1% (m_q/m_v of 2.0). The deviations were even more widespread for the ACs, spanning between 50.2% (m_q/m_v of 0.5) and 52.7% (m_q/m_v of 2.0). These deviations are attributable to the complex interactions that typically occur between pyrolysis volatiles and the QM, which are difficult to accurately represent in the theoretical model. The known limitation of the UNIFAC-DMD model's inability to accurately predict infinite dilution of organic compounds in water is also largely accountable for the even more weighty deviations observed for the case of the AC [31,35]. In addition, the uncertainties surrounding the pure component vapour pressure data for some of the surrogate compounds are key factors that are responsible for the deviations observed. Nonetheless, it is noteworthy to mention that, regardless of the deviations, qualitative trends of the models were generally comparable with experimental data.

3.2. *Effects of quench media type on composition of FPBOs*

3.2.1. *Effects on moisture content of the ORC*

3.2.1.1. Experimental investigations. The moisture content of the ORC significantly affects FPBO quality. It defines some key physicochemical properties (such as viscosity and calorific values) of the ORC and it is also decisive for its stability. Effects of QM type on the moisture content of the FPBOs have been presented in Fig. 4a. For m_q/m_v of 2.0, water content detected in the ORCs were about 10, 14, 7 and 15 wt% for Isopar-V, water, glycol and ethanol, respectively. These figures are

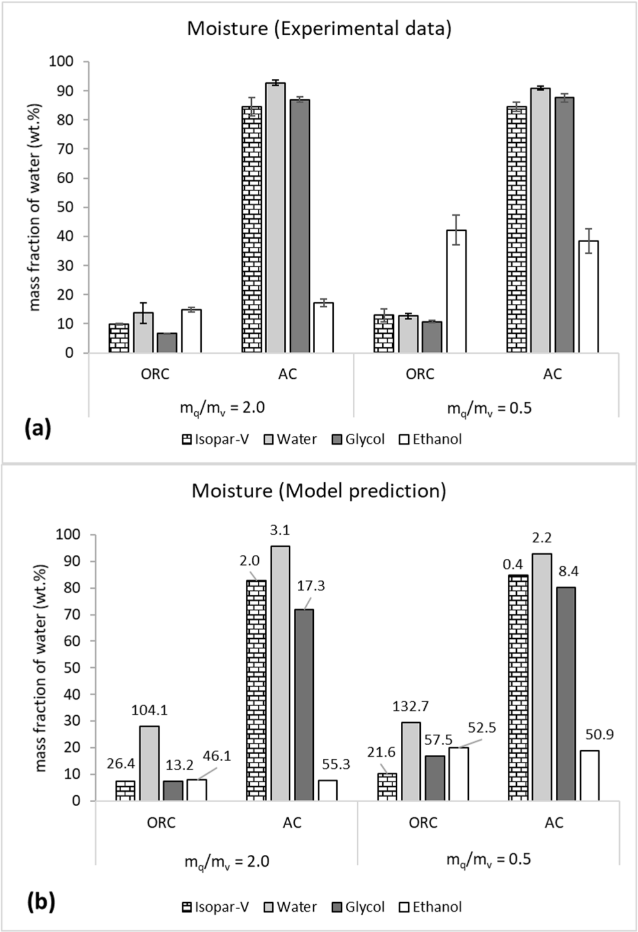

Fig. 4. Moisture content of FPBOs (ORC and AC) based on the effects of all QM: (a) experimental data and (b) model predicted data showing individual absolute relative deviations (ARDs) with respect to experimental data. Moisture content was reported on 'as received' basis.

consistent with the range usually reported for ORCs derived from ash-rich biomass feedstocks such as wheat straw [34,36]. A similar range of figures were also recorded for m_q/m_v of 0.5, except that at this condition, significantly high amounts of moisture (about 42 wt%) were recorded for the ethanol quench scenario. This hints of strong interactions between water and ethanol during quenching, where augmented supply of ethanol quench means an increased interaction with and consequent absorption of water by ethanol leading to less moisture in the resulting ORC as evidenced in the m_q/m_v of 2.0 scenario.

3.2.1.2. Model predictions. Generally, model predictions (Fig. 4b) were very comparable to experimental data. ORC AARDs of 66.1 and 47.5% were recorded for m_q/m_v of 0.5 and 2.0, respectively. It is however noteworthy to highlight the significantly high ARD of the water-quench scenario, which significantly contributed to the increased AARDs recorded for the ORC. Water as an exceedingly high polar compound has higher tendencies of undergoing association and hydrogen bonding interactions with condensing volatiles and with the UNIFAC-DMD model being limited in accurately predicting such complex interactions, the conspicuous deviations observed for this quench scenario are not surprising.

As expected, moisture content of all corresponding ACs for all QM, bar ethanol were higher than 80 wt% regardless of m_q/m_v. The dramatic lower figures recorded for ethanol ascertains the absorption of water by this quench during condensation. Model predicted Txy data (Fig. S1 of supplementary information) revealed the formation of an azeotrope between water and ethanol at around the boiling point temperature of ethanol (78.14 °C), establishing the prospects of inseparable water vapour from uncondensed ethanol and hence the conspicuous decrease in moisture content in the resultant AC.

Like ORCs, the model predictions for ACs were also very comparable with experimental data (Fig. 4b), recording even lower AARDs that only extended between 15.5% (m_q/m_v of 0.5) and 19.4% (m_q/m_v of 2.0). Nonetheless, ARDs for ethanol were quite extensive and once again highlights the limitations of the UNIFAC-DMD model in accurately predicting typically high association systems that exist between water and ethanol.

3.2.2. Effects on the distribution of major functional group compounds in FPBOs

The investigated QM affect the composition of the recovered condensates (ORC and AC). The selectivity of QM towards this is presented and discussed based on the distribution of major functional groups present in the condensates. In Figs. 5 to 8, both experimental data and theoretical predictions of the selectivity fingerprints are shown on dry and QM-free basis relative to the total amount of volatiles that enter the first condensation stage. Average standard deviations for the mass fractions (experimental data) of all functional groups were less than 0.20 wt% for ORC and 0.05 wt% for AC.

3.2.2.1. Experimental investigations. As previously mentioned, Isopar-V formed an immiscible product with the recovered ORC. For this QM, carboxylic acids (primarily comprising of acetic and propionic acids) were the most dominant detectable fractions in its ORC (Fig. 5a), with mass fractions (concentrations) of a little below 2 wt% detected for both m_q/m_v ratios. Nonaromatic ketones (chiefly comprising of acetol, 2-butanone and cyclopentanone) were the most dominant fraction after carboxylic acids, with concentrations of about 1.25 wt% at m_q/m_v of 0.5 and 0.80 wt% at m_q/m_v of 2.0. Lignin-derived phenols (mostly including phenol and o,m,p-cresols) and guaiacols were also present in substantial amounts in the ORC, with their concentrations ranging between 0.46 and 0.83 wt% across both m_q/m_v ratios. These were followed closely by andydrosugars (particularly levoglucosan) and syringols, all recording mass fractions of about 0.45 wt% (m_q/m_v of 0.5) and 0.32 wt% (m_q/m_v of 2.0). Furans (mostly constituting furfural, 2(5H)-furanone and 2-furfural alcohol) and non-aromatic alcohols were among the compounds with the least concentrations detected in the ORC. Their fractions ranged between 0.14 and 0.32 wt%. No aldehydes were detected in the ORCs.

As deduced for the ORC, nonaromatic ketones and carboxylic acids also formed the most dominant constituents of the AC recovered at both ratios of m_q/m_v (Fig. 5b). Relative to these, alcohols, furans, lignin-derived phenols, guaiacols and syringols were detected in trace amounts. No sugars were present in the AC. Unlike the ORC, some trace amounts (0.01 to 0.02 wt%) of nonaromatic aldehydes (customarily made up of compounds such as hydroxyacetaldehyde and crotonaldehyde) were detected in the AC.

It is noteworthy to mention that fractions of aliphatic hydrocarbons (mostly comprising of C_{14} to C_{17} alkanes) were also detected in both FPBOs (ORC and AC). The detected alkanes were similar in composition to the ones typically present in Isopar-V, illustrating that some fractions of the quench were retained in the FPBOs. This is consistent with the losses recorded for the total Isopar-V quench that was originally supplied (Table 3). Inversely, some trace amounts of all characterised functional group compounds typically present in FPBOs were also detected in the recovered spent Isopar-V quench, affirming mass transfer of components between both phases. Mazerolle et al. [20] and Zacher et al. [21] who also employed Isopar-V in condensing their hot pyrolysis vapours made similar inferences.

For the water quench scenario (which was also immiscible with the ORC), the mass fractions of acids and ketones were not as conspicuous in

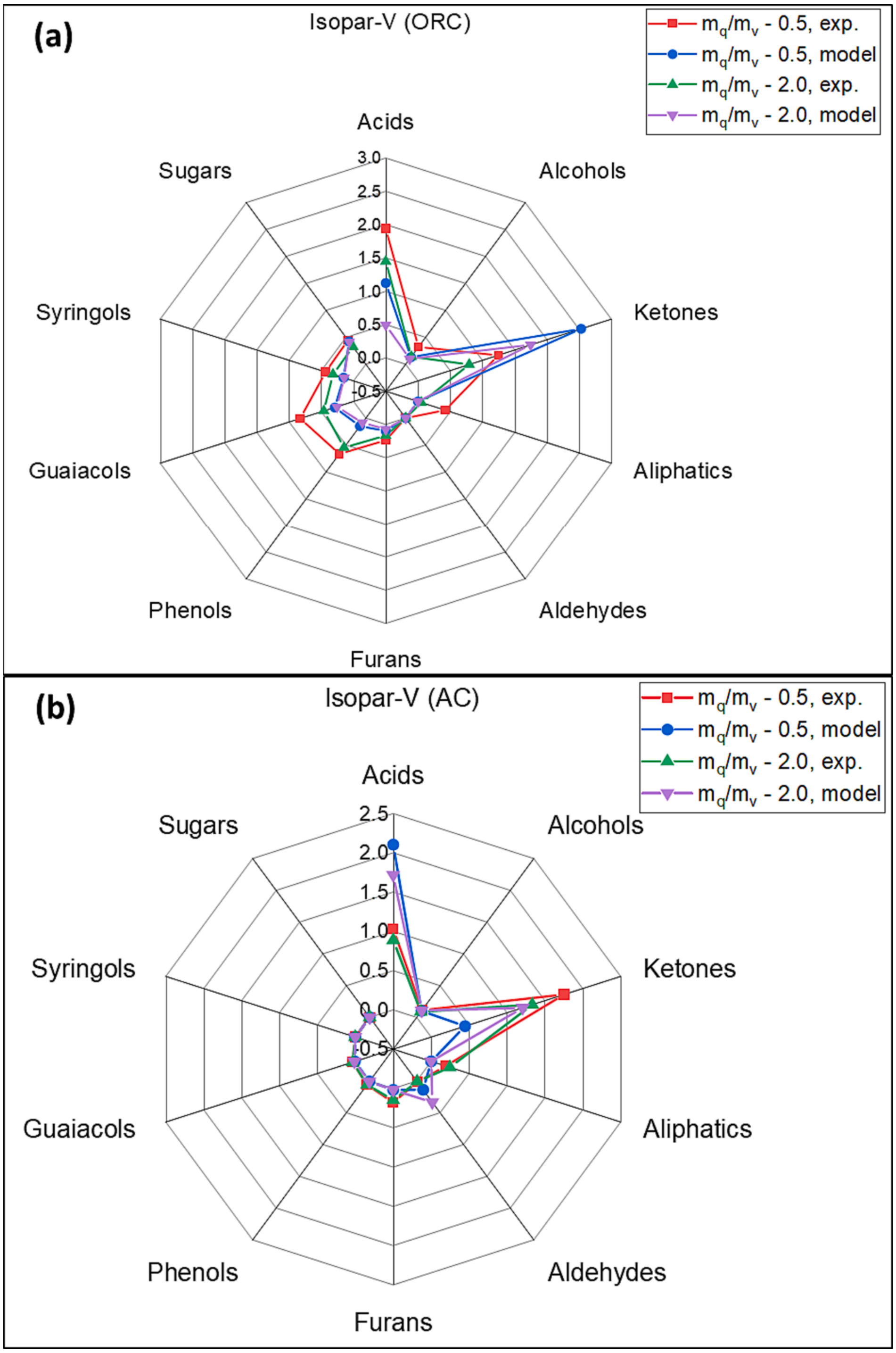

Fig. 5. Effects of Isopar-V QM on the mass fractions of major functional group compounds in FPBOs showing distributions for model predictions: (a) ORC and (b) AC. Mass fractions for FPBO components are with respect to total pyrolysis volatiles entering the first condensation stage.

the ORC like they were for the case of the Isopar-V quench (Fig. 6a). Acid concentrations of 0.57 wt% (m_q/m_v of 0.5) and 0.47 wt% (m_q/m_v of 2.0) were recorded in the ORC besides ketone concentrations of 0.59 wt% (m_q/m_v of 0.5) and 0.32 wt% (m_q/m_v of 2.0). Unlike the case of the Isopar-V quench, no aliphatic hydrocarbons were detected in the ORC, ascertaining the fact that those detected for Isopar-V were directly from the QM. Notably, phenolic compounds (lignin-derived phenols, guaiacols and syringols) were also detected in substantial amounts in the ORC relative to acids and ketones with their concentrations spanning between 0.45 and 0.67 wt% for both m_q/m_v ratios (Fig. 6a). With water being a highly soluble solvent for most compounds in the FPBO such as sugars, ketones and acids, employing water as quench, would imply that most of these water-soluble compounds are transferred into the spent water QM (extract) phase, thereby concentrating heavier molecular weight compounds such as the lignin-derived phenols and compounds alike (guaiacols and syringols) in the ORC. The transfer of water-soluble compounds into the spent water QM is evident in the conspicuous concentrations of acids and ketones (most especially for the m_q/m_v of 2.0 ratio) that ended up in this phase (Fig. 6c). At this m_q/m_v ratio, close to 200 and 155 wt% increase in the concentrations of acids and ketones

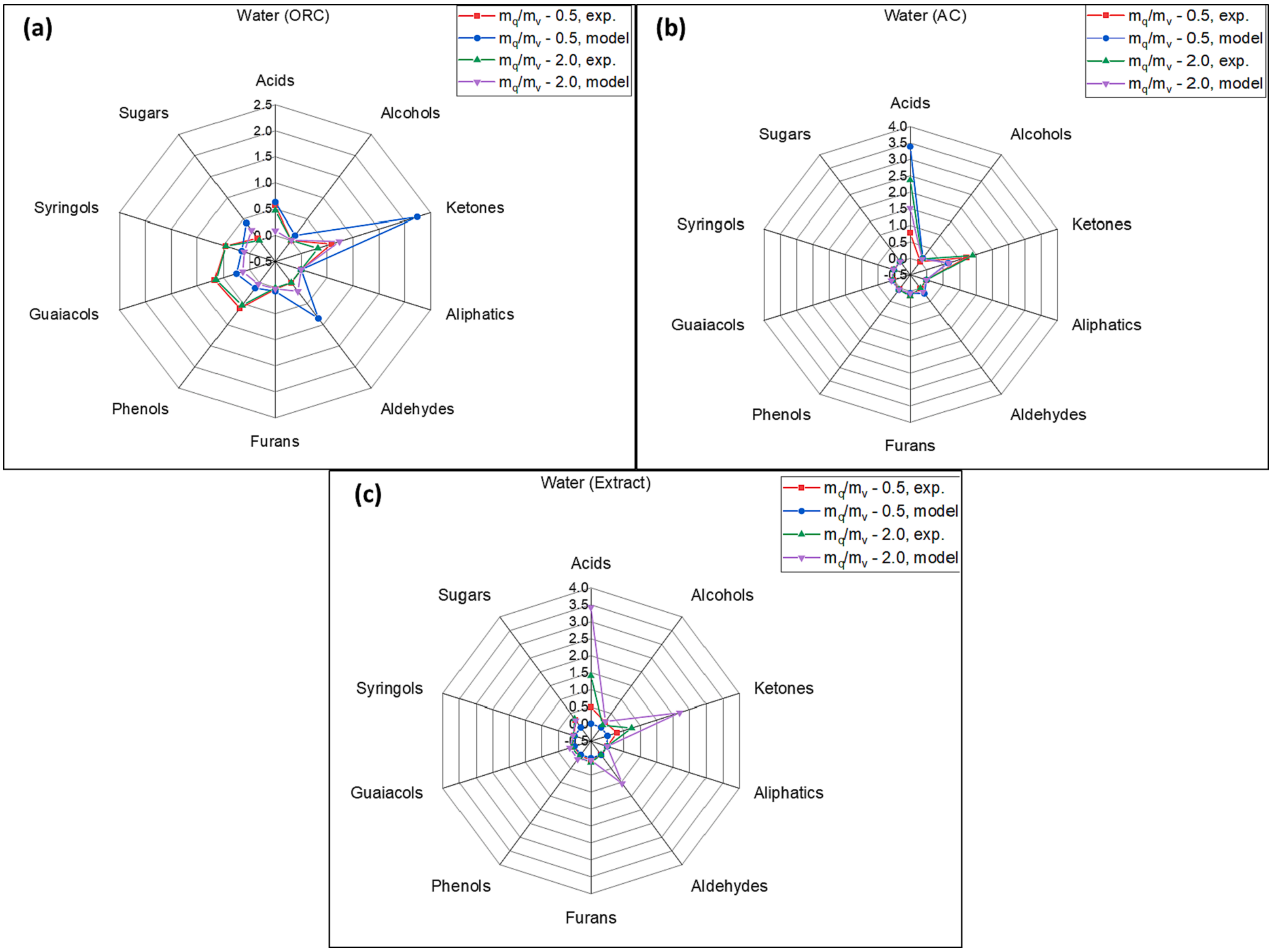

Fig. 6. Effects of Water QM on the mass fractions of major functional group compounds in FPBOs showing distributions for model predictions: (a) ORC, (b) AC and (c) Phase separated spent water QM (extract) from ORC fraction. Mass fractions for FPBO components are with respect to total pyrolysis volatiles entering the first condensation stage.

relative to their concentrations in the ORC were detected in the recovered spent quench, respectively. Also, nearly all sugars ended up in this phase. For the 2.0 m_q/m_v ratio, 100% of generated sugars were recovered in the spent water QM. This is prospective for sugar extraction in a single step quenching condensation process. Alcohols were also present in the recovered quench with their concentrations ranging from about 0.08 (m_q/m_v of 2.0) to 0.20 wt% (m_q/m_v of 0.5). Lignin-derived phenols, guaiacols and syringols were only detected in trace amounts (with concentrations below 0.1 wt% at all conditions of m_q/m_v) in the spent water QM.

Product distribution of the compounds retrieved in the ACs of the water-quench scenario was very similar to that of Isopar-V, with ketones (1.30 wt% on average) and acids (0.82 wt% on average) forming the most prevalent fractions (Fig. 6b). Like the ORC, no aliphatic compounds were present, further substantiating the fact that those detected in the AC for the Isopar-V quench were sourced from the QM. Again, sugars were absent and in relative to the acids and ketones, the remaining compounds were present in minute concentrations. With the increased condensation of water on the second condensation stage, the tendencies of these compounds being present in only trace amounts is very much expected.

All the QM that formed homogeneous mixtures with the ORCs (glycol and ethanol) recorded the highest fractions of acids and ketones in the ORC (Fig. 7a & Fig. 8a). Acid concentrations ranged from around 4.0 wt% (m_q/m_v of 0.5) to 7.5 wt% (m_q/m_v of 2.0) for ethanol. For glycol, a concentration of 10 wt% was recorded at m_q/m_v of 0.5. It is important to mention that no acids were originally detected in the ORC of glycol $m_q/m_v = 2.0$ scenario, owing to the severe dilution of this product by the quench, which led to concentrations below quantification limits of the GC-FID/MS. The substantial concentration of acids (ca. 0.50 wt%) in its corresponding AC (Fig. 7b) ascertains this. Ketone concentration spanned from about 7.0 wt% ($m_q/m_v = 0.5$) to 17.0 wt% ($m_q/m_v = 2.0$) for glycol and 4.50 wt% ($m_q/m_v = 0.5$) to 6.60 wt% ($m_q/m_v = 2.0$) for ethanol. Treedet et al. [12] made comparable observations when they employed ethanol as quench for the condensation of pyrolysis volatiles generated from Napier grass, sugarcane and rubber leaves, where they reported dominant concentrations of carboxylic acids in relation to the other detected compounds in the ORC.

Furthermore, the ORC recovered by the glycol quench generated the highest fractions of lignin-derived phenolic compounds (phenols, guaiacols and syringols) in comparison to all the other investigated QM. Their concentrations in this product were on average, about four times greater than in the corresponding ORCs recovered using ethanol and five times greater than ORCs recovered using Isopar-V and water. The concentrations of these compounds in corresponding ACs recovered using the glycol-quench were virtually negligible.

For both QM, most especially for glycol, it was also noted that the concentrations of most compounds (particularly acids and ketones)

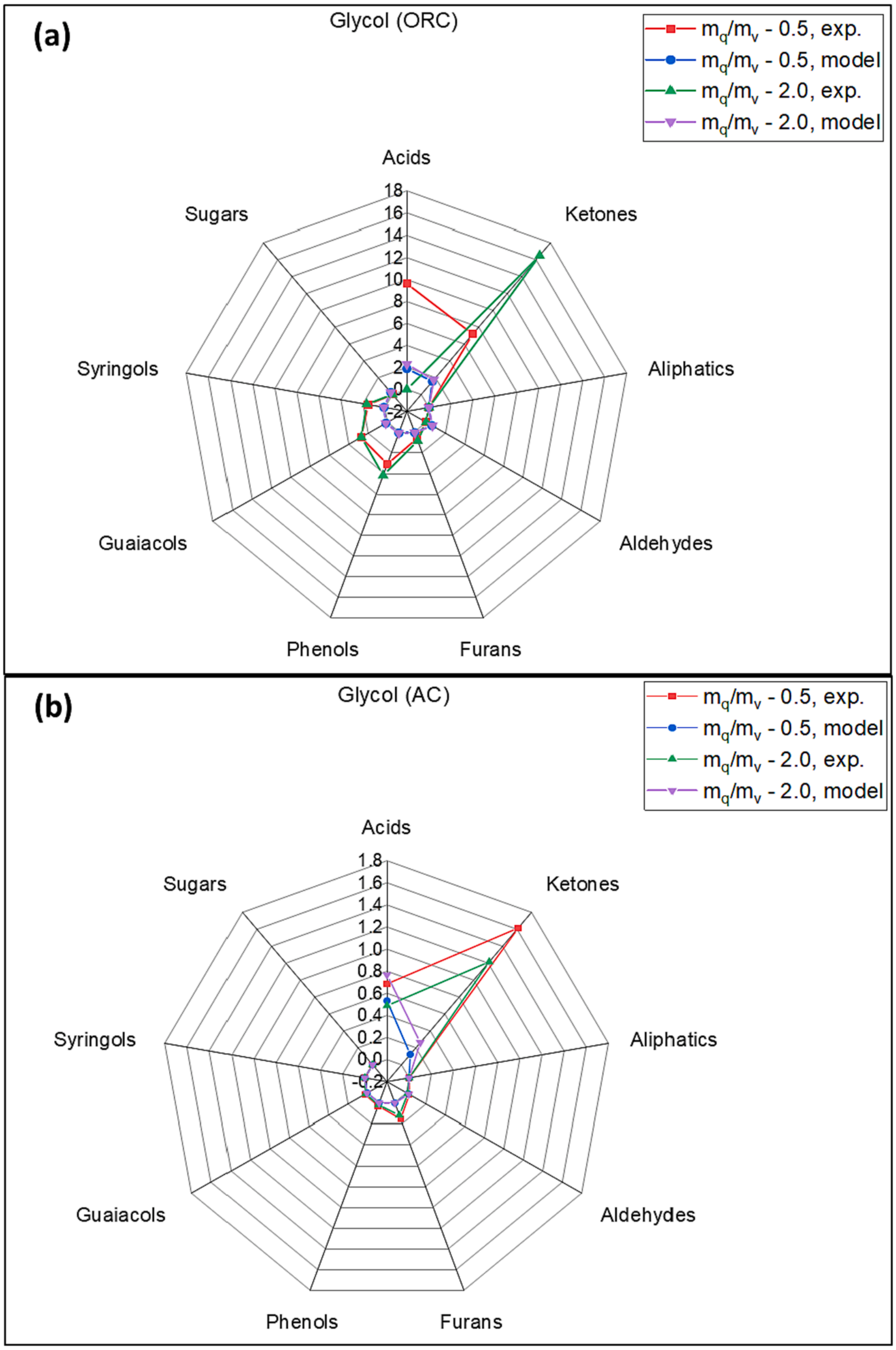

Fig. 7. Effects of Glycol QM on the mass fractions of major functional group compounds in FPBOs showing distributions for model predictions: (a) ORC and (b) AC. Mass fractions for FPBO components are with respect to total pyrolysis volatiles entering the first condensation stage.

detected in the ORC were greater for the m_q/m_v of 2.0 ratio than for the m_q/m_v of 0.5 ratio. Similar observations were also made for the Isopar-V quench. This indicates that higher mass ratios of these organic QM (ethanol, Isopar-V and glycol) to the pyrolysis volatiles, which also implies lower condensation temperatures enhanced the condensation and recovery of most compounds in the ORC. This was however not the case for the water-quench as most of these compounds were soluble in water and instead ended up in the spent water-quench phase.

Ketones constituted the most dominant organic compound in the ACs recovered using ethanol and the glycol quench. Concentrations of 1.62 wt% ($m_q/m_v = 0.5$) and 1.22 wt% ($m_q/m_v = 2.0$) were recorded for glycol whereas concentrations of about 1.30 wt% (at both m_q/m_v ratios) were noted for the ethanol quench (Fig. 7b & Fig. 8b). Concentrations of acids were also present in substantial amounts of 0.68 wt.% ($m_q/m_v = 0.5$) and 0.49 wt% ($m_q/m_v = 2.0$) for glycol besides 0.33 wt% ($m_q/m_v = 0.5$) and 0.20 wt% ($m_q/m_v = 2.0$) for ethanol. For both QM, aldehydes, furans, phenols and guaiacols were identified in trace amounts. Nonetheless, sugars and syringols were not detected in the AC.

3.2.2.2. Model predictions compared with experimental data. Model predictions of the concentrations of all the major functional group

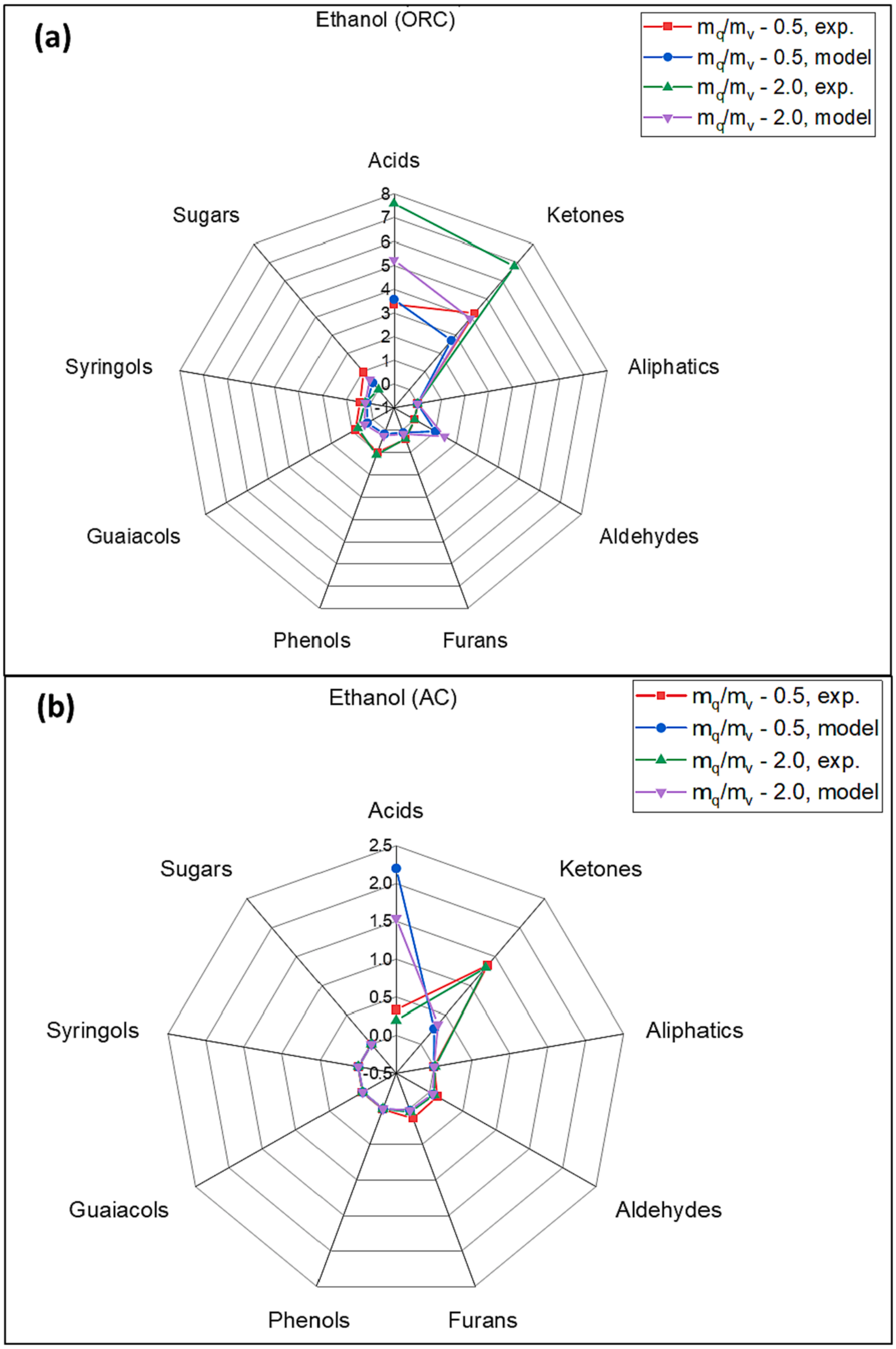

Fig. 8. Effects of Ethanol QM on the mass fractions of major functional group compounds in FPBOs showing distributions for model predictions: (a) ORC and (b) AC. Mass fractions for FPBO components are with respect to total pyrolysis volatiles entering the first condensation stage.

compounds present in the FPBOs generally followed similar qualitative trends as experimental data (Figs. 5 to 8). Notwithstanding, some significant deviations were also noted, most especially with predictions of the ACs and the cases where water was employed as quench, explicable to the limitation of the UNIFAC-DMD model in accurately predicting highly dilute concentrations of organic compounds in water.

AARDs of all functional groups at all process conditions have been presented in Table 4. For all QM investigated, model predictions of the major functional group compounds present in the ORCs deviated the least as compared to their counterparts in the ACs. For the ORC products, the ethanol-quench scenario recorded the least AARD (about 50%

Table 4
Average absolute relative deviations (AARDs) (%) of major functional groups present in FPBOs for all QM investigated.

Quench	ORC		AC	
	$m_q/m_v - 0.5$	m_q/m_v-2.0	m_q/m_v-0.5	m_q/m_v-2.0
Isopar-V	64	65	146	407
Water	182	124	439	352
Glycol	89	93	72	74
Ethanol	56	42	154	155

on average), followed by Isopar-V (64% on average) and glycol (90% on average). Water-quench scenario recorded the highest AARD, averaging a little over 150%. With water being a polar compound, it typically undergoes complex association interactions such as solvation and hydrogen bonding interactions for which the UNIFAC-DMD reportedly does not consider [37]. Most especially for the AC products, the UNIFAC-DMD model is also characterised with its limitation of accurately handling infinitely dilute hydrocarbons in water, and with the AC considerably diluted with the water QM, the significantly higher deviations observed (as compared to ORC) are unsurprising.

To establish the selective recovery of the yields and chemical compositions of the ORCs and the ACs, the corresponding ratios (for product yield and composition) of ORC to AC were calculated for both experimental and model predicted data (Tables S2 to S6 of supplementary information). Comparing the deviations of model predicted ratios to experimental data also permitted for further comparisons between these two datasets. It was deduced from the data presented that although fairly significant differences were seen between experimental and model predicted ratios, their qualitative trends were still generally well replicated. Interestingly, product yield and composition ratios of experimental and corresponding model predicted data were all above unity, suggesting that significant yield of the condensed volatiles were recovered as ORC with a majority fraction of the compounds also being retained in this fraction. Notably, the recovery of sugars solely in the ORC as per experimental findings was accurately reproduced by the model predictions.

3.2.3. Model prediction of the ORC as quench relative to all investigated QM

To ascertain how all the investigated QM in this study compare with the technique of using the ORC as quench (a common practice for industrial scale pyrolysis systems), the UNIFAC-DMD model was used to simulate the yield distribution and composition of FPBOs by employing the ORC as quench. Only theoretical model predictions were considered because the PDU used in this study has not been fully designed and optimised to classically execute such a process.

Compared to the model predictions of all the other investigated QM, it was revealed that m_q/m_v ratios for the ORC as quench case barely affected the yield distribution of the recovered FPBOs (Table 5). On average, the yield of recovered ORC (25.4 wt%) was greater than yields recovered using water and glycol (ca. 16 wt%) as quench, comparable to yield recovered using Isopar-V (ca. 25 wt%) and less than the yield recovered using ethanol (ca. 32 wt%). Furthermore, AC yield obtained using this quench was comparable to the AC yields obtained for all the other investigated QM.

Average moisture content of ORC recovered was about 27 wt% (Table 6), which is more comparable to that recorded when water was employed as quench. Identical to the cases of Isopar-V, water and glycol, moisture content of the recovered AC (employing ORC quench) was at least 80 wt%.

Distribution of mass fractions in the respective FPBOs have been represented in Fig. 9. Acids and ketones formed the most dominant fraction in the ORC recovered using ORC as quench. Concentrations of acids were about 2.0 wt% (m_q/m_v of 0.5) and 3.5 wt% (m_q/m_v of 2.0). Mass fraction of ketones were congruent with the ones recorded for acids. Aldehydes formed the next dominant fraction after acids and ketones with concentrations of about 1.0 wt% ($m_q/m_v = 0.5$) and 1.5 wt%. ($m_q/m_v = 2.0$). Relative to these compounds, furans, phenols, guaiacols, syringols and sugars were only detected in trace amounts. The qualitative distribution trends of these compounds are mainly comparable with those observed for the Isopar-V quench. The AC only primarily contained acids of about 2 wt% for both m_q/m_v ratios. Unlike for the cases of all the other investigated QM, ketones were present in comparatively small amounts in the AC.

Table 5
Model predicted yield distribution (in wt.%) of ORC and AC obtained following condensation using ORC quench. Yields reported on dry and QM-free basis.

m_q/m_v − 0.5		m_q/m_v − 2.0	
ORC	AC	ORC	AC
25.8	2.2	25.0	2.4

Table 6
Model predicted moisture content (in wt.%) of ORC and AC obtained following condensation using ORC quench. Moisture content reported on “as received” basis.

m_q/m_v − 0.5		m_q/m_v − 2.0	
ORC	AC	ORC	AC
26.5	80.9	28.3	79.7

3.2.4. Reflections on shortcomings of model predictions

Generally, the UNIFAC-DMD model has proved to a greater extent a promising model for predicting the highly non-ideal vapour-liquid equilibrium behaviour of fast pyrolysis vapours. Nonetheless, some noteworthy deviations of qualitative trends were observed, most especially for the prediction of chemical composition. These were attributable to short-comings of the model that include, (i) its inability to copiously handle highly dilute organics in water, (ii) its limitation of accurately predicting some specific association and hydrogen bonding interactions and (iii) effects of uncertainties of pure component vapour pressure data associated with several of the chemical compounds that constitute the pyrolysis vapours, which were only estimated theoretically owing to the unavailability of experimental data. In view of this, more complex thermodynamic models such as the group contribution with association equation of state (GCA-EoS), which have been reported by Ille et al. [37] to mitigate the above outlined setbacks, ought to be considered.

In essence, model prediction of the quenching condensation process using the UNIFAC-DMD model was not without setbacks, however, its implementation in this study obviously provides intriguing addition towards further understanding the condensation process and consequently, the challenges unearthed are paramount for detailed parametric studies for quenching condensation systems. Inasmuch as quenching condensation is a complex process that encompasses highly dynamic heat and mass transfer phenomena, this study was solely focussed on phase equilibria since it is an essential pre-requisite towards investigating actual dynamic systems, helping towards understanding fundamental aspects of process design and its influence on product quality.

4. Conclusions

It was shown that the choice of quench media (QM) alters the characteristics and composition of resultant fast pyrolysis bio-oils (FPBOs). Ethanol recovered the highest yield of the organic-rich condensate (ORC) fraction of the FPBOs, most particularly at a mass flowrate ratio of the quench to hot pyrolysis volatiles (m_q/m_v) of 2.0, which produced 50 wt% more ORC than ethylene glycol and 75 wt% more than water and Isopar-V. Ethylene glycol recovered the highest fractions of major chemical compounds that include carboxylic acids, ketones and phenolics in the ORC. Isopar-V largely demonstrated immiscibility with the ORC, however, some slight interactions with the ORC product were evident. For the water quench, owing to its significant interactions with the ORC, nearly all water-soluble compounds, particularly sugars were transferred into this quench following condensation, making it valuable for the recovery of sugars directly from pyrolysis vapours during quenching. As ethanol and ethylene glycol form a homogeneous mixture with the ORC, arduous and costly downstream

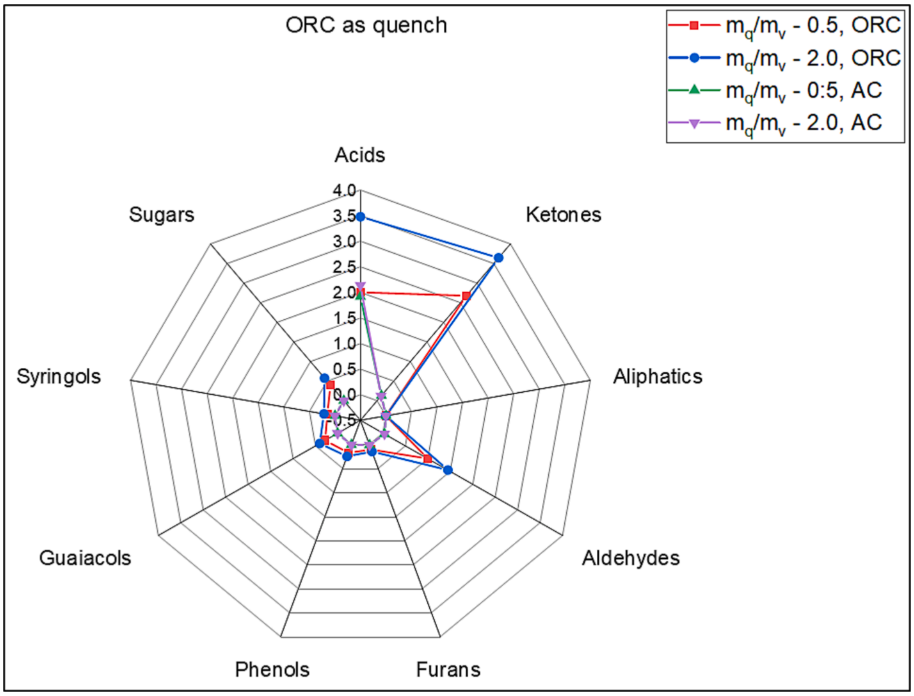

Fig. 9. Model predicted effects of ORC quench on the mass fractions of major functional group compounds in FPBOs.

separation methods may be required to isolate these QM from their corresponding ORCs. Phase equilibria simulation of all the quenching condensation processes investigated employing the modified UNIFAC Dortmund (UNIFAC-DMD) thermodynamic model demonstrated huge prospects, most specifically in predicting the yield and composition of the ORC. However, it was not without setbacks as the limitations of the model was exposed in scenarios of modelling low concentrations of organics in water, association and hydrogen bonding interactions and uncertainties associated with pure component vapour pressure data of some compounds. In that regard, more advanced models such as the group contribution with association equation of state (GCA-EoS) are to be considered for future studies.

CRediT authorship contribution statement

George Kofi Parku: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Visualization. **Axel Funke:** Writing – review & editing, Visualization, Supervision, Funding acquisition, Conceptualization. **Nicolaus Dahmen:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.126873.

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