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D6.2 - EHL-derived molecular surrogate compositions

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Summary

Deliverable 6.2 is the second one in task 6.1, whose goal is to characterize the composition of the fuels derived from enzymatic hydrolysis lignin (EHL) and to define the associated molecular substitutes. The first step is to identify the most important chemical species that present in EHL-derived solvolysis oil though bibliographic study and experimental analysis using two-dimensional gas chromatography (GC-2D) of samples provided by the EHLCATHOL partners. The results of the characterization are of particular importance in the case of the biofuels in the EHLCATHOL project and makes it possible to propose molecular substitutes, which represent the main families of chemical species to study the combustion properties on solvolysis oil.

Following the bibliographical review presented in Deliverable 6.1, which provided, in addition to an introduction on biomass valorisation, a bibliographical study on EHL-derived fuels combustion properties (BP, MP, RON and CN...), and a review on the kinetic works related to the gas-phase reactions of the main oxygenated aromatics expected in the biofuel composition, **the first part of Deliverable 6.2** reports on the kinetic works related to the gas-phase reactions of arenes (toluene, styrene, xylenes isomers, ethyl benzene, trimethylbenzene isomers, propyl benzene) present in EHL-derived fuels. The structure of the molecules considered in this part is given in Table 1.

Based on the analysis of samples respectively provided by Vertoro and Aalto, **the second part of Deliverable 6.2** describes the obtained composition of two representative EHL-derived fuels, showing significant amounts of oxygenated aromatics, especially phenolic compounds.

Based on the bibliographical and analytical results reported in Deliverables 6.1 and 6.2 and on discussion with Aalto and Vertoro, **the third part of Deliverable 6.2** details the molecular composition of the surrogates proposed to represent EHL-derived fuels in the experimental work to be performed in tasks 6.3 and 6.2.

A **fourth part** concludes on the work performed in task 6.1.

Table 1: Structure of aromatic oxygenates, for which kinetic studies are available.

Chemical name	The structure		
Toluene	CH ₃		
Styrene	CH ₂		
o, m, p-xylene			
Ethylbenzene			
Propylbenzene	CH ₃		
1,3,5-trimethylbenzene	CH ₃ CH ₃ CH ₃ CH ₃		
1,2,4-trimethylbenzene	H ₃ C CH ₃		



1.Bibliographic review of the kinetic work related to the gas-phase reactions of arenes

In this part are considered pyrolysis, oxidation as well as flame combustion. The mentioned experimental set-up not involving flame are flow and jet-stirred reactors, shock tubes and rapid compression machine to measure the profile of species mole fractions or ignition delay times. The flame set up are constant volume or pressure bombs and different types of burners to measure Laminar Burning Velocity (LBV) or the profile of species mole fractions.

1.1. Toluene

As is shown in Tables 2 and 3, a significant number of studies were made about the gas-phase reaction of toluene. Its oxidation has been studied in flow reactors since 1984 by Brezinsky and his team (1–3). The experiments were performed in a turbulent flow reactor at 1 atm, 1200 K and equivalence ratios from 0.69 to 1.33 using gas-chromatography (GC) coupled with and mass spectrometry (MS) analysis. Based on these results, they developed a model contains 529 reactions and 97 chemical species. In 2011, Metcalfe et *al.* (4) used also a turbulent flow reactor for the oxidation of toluene at 12.5 atm over a temperature range 600-1000 K. They used their results to develop a detailed chemical kinetic mechanism including 329 species and 1888 reactions for toluene oxidation and the intermediates of its combustion. They showed that the main products were CO, CO_2 , C_2H_4 and benzene.

In 1987, Pamidimukkala et *al.* (5) studied the pyrolysis of toluene using a shock tube at various pressures (P = 0.2-0.5 atm) over a range temperatures of T =1550-2200 K. The main major products obtained were CO, acetylene, methane, ethylene, and benzene. After that, Braun-Unkhoff et *al.* (6) investigated the thermal decomposition of toluene between 1 and 7 atm, over a temperature range of 1300 and 1800 K. The work of Sivaramakrishnan et *al.* (7,8) was performed behind reflected shock waves using a single pulse shock tube at 27 and 45 atm over a wide temperature range (1200–1900 K). The major stable species detected and quantified were CO, C_2H_2 , CO_2 , C_2H_4 and benzene using GC combined with MS.

A more recent work on the pyrolysis of toluene was performed by Zhang et *al*. (9) in a flow reactor at 0.013 atm in the temperature range of 1200–1800 K using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). This technique can help distinguish most isomers, and reduce fragmentation via near-threshold photoionization, allowing unambiguous detection of radicals. Using the same methods, Yuan et *al*. (10,11) worked at pressures from 0.0066 to 1 atm and temperatures from 1100 to 1730 K. They identified a large range of products with GC (CO, CO₂, C₂H₄, C₄H₄, styrene and ethylbenzene).

Shock tubes were also used to measure toluene ignition delay times. The first study was performed in 2005 by Vasudevan et *al.* (12) at low-pressure (P=1.5-5 atm) and low O₂ concentration (0.225–0.5% O₂). The same year, Davidson et *al.* (13) measured ignition times for toluene/air mixtures in a shock tube at pressures from 14 to 59 atm. Finally, Shen et *al.* (14) also evaluated the ignition delay times of toluene between 1021-1400 K, but at high pressures (P=12-50 atm) to resolve the disagreements in ignition delay time and pre-ignition energy release behaviour between the data of Davidson et *al.* (13) and those Mittal and Sung (15) measured in a rapid compression machine.



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Table 2: Summary of the main experimental studies about toluene (neat fuel).

Instrument	Measured property	Experimental Conditions	Reference
		T=1180 K ; Φ=0.76, 1.4; P= 1 atm.	Brezinsky et <i>al.</i> , (1984, 1990) (1,2)
		T=1173 K ; Φ=0.76; P= 1 atm.	Klotz et <i>al.,</i> 1998 (3)
Flow reactor		T= 420-950 K; Φ= 0.6-1.5; P= 12.5 atm	Metcalfe et <i>al.,</i> 2011 (4)
		T= 1200-1800 K; P= 0.013 atm	Zhang et <i>al.,</i> 2009 (9)
	Species profiles	T=1100-1730 K ; Φ=∞; P=0,0066-1 atm.	Yuan et <i>al.,</i> 2016 (10,11)
		T=1150-2200 K ; Φ=∞; P=0.2-0.5 atm.	Pamidimukkala et <i>al.,</i> 1987 (5)
		T=1300-1800K ; Φ=∞; P=1-7 atm.	Braun-Unkhoff et <i>al.,</i> 1989 (6)
Shock tube		T=1200-1900 K ; Φ=∞; P=27- 45 atm.	Sivaramakrishnan et <i>al.,</i> (2004, 2006) (7,8)
	Ignition delay times	T = 1430-1820 K ; Φ = 1; P = 1 atm.	Vasudevan et <i>al.,</i> 2005 (12)
		T = 1000-1320 K; Φ = 0. 5-1; P = 50 atm.	Davidson et <i>al.,</i> 2005 (13)
		T = 1110-1420 K ; Φ = 0.25-1; P = 12-50 atm.	Shen et <i>al.,</i> 2009 (14)
Rapid compression machine		T = 920-1100 K ; Φ = 0.5-1; P = 25-40 atm.	Mittal and Sung (15)
		T=1000-1400 K ; Φ=0.5,1,1.5; P=0.98 atm.	Dagaut et <i>al.,</i> 2002 (16)
Jet-stirred reactor	Species profiles	T=873-923 K ; Φ=0.45,0.91; P=0.98 atm.	Bounaceur et <i>al.,</i> 2004 (17)
		T=950-1200; Φ=0.5, 1.0, 1.5; P=9.86 atm.	Yuan et <i>al.,</i> 2016 (10)





$\label{eq:table 3} \textbf{Table 3}: Main experimental kinetic studies about toluene flames. \ T_{fg} is the fresh gas temperature.$

Instrument	Measured property	Experimental Conditions	Reference
		T _{fg} =298 K ; P=1 atm ; Φ=0.7-1.3	Davis et <i>al.,</i> 1996 (18), Davis et <i>al.,</i> 1998 (19)
		T _{fg} =298 K ; P=1 atm ; Φ=0.8-1.3	Hirasawa et <i>al.,</i> 2002 (20)
		T _{fg} =400, 470 K ; P=1 atm ; Φ=0.7-1.4	Kumar et <i>al.,</i> 2010 (21)
Counter Flow burner		T _{fg} =403 K ; P=1 atm ; Φ=0.7-1.4	Ji et <i>al.,</i> 2011 (22)
		T _{fg} =353 K ; P=1 atm ; Φ=0.7-1.5	Ji et <i>al.,</i> 2012 (23)
		T _{fg} =400, 470 K ; P=1 atm ; Φ=0.7-1.4	Hui et <i>al.,</i> 2012 (24)
		Т _{fg} =400 К ; Р=1-3 atm ; Ф=0.7-1.4	Hui et <i>al.,</i> 2013 (25)
		T _{fg} =450 K ; P=3 atm ; Φ=0.8-1.4	Johnston et <i>al.,</i> 2005 (26)
Constant Volume	Laminar burning velocity	T_{fg} =358, 423 K ; P=1 atm ; Φ=0.7-1.5 T_{fg} = 423 K ; P=1-20 atm ; Φ=0.6-1.5	Wang et <i>al.,</i> 2017 (27)
Chamber		T _{fg} =400, 450 K ; P=1, 3 atm ; Φ=0.6-1.5	Zhong et <i>al.,</i> 2018 (28)
Constant Pressure Chamber		T _{fg} =393, 433 K ; P=1 atm ; Φ=0.7-1.5	Zhang et <i>al.,</i> 2019 (29)
		T _{fg} =353 K ; P=1-5 atm ; Φ=0.7-1.7	Han et <i>al.,</i> 2017 (30)
		T _{fg} =400 K ; P=1 atm ; Φ=0.6-1.5	Munzar et <i>al.,</i> 2013 (31)
Bunsen		T _{fg} =423 K ; P=1 atm ; Φ=0.6-1.3	Wu et <i>al.,</i> 2017 (32)
		T _{fg} =298, 358 K ; P=1 atm ; Φ=0.7-1.3	Sileghem et <i>al.,</i> 2013 (33)
		T _{fg} =298 - 398 K ; P=1 atm ; Φ=0.55-1.55	Dirrenberger et <i>al.,</i> 2014 (34)
		T _{fg} =298 K ; P=1 atm ; Φ=0.8-1.3	Liao et <i>al.,</i> 2016 (35)
		T _{fg} =273 K ; P=30 Torr ; Φ=1.9	Li et <i>al.,</i> 2009 (36)
Flat flame burner		T _{fg} =298 K ; P=36 Torr ; Φ=2	Detilleux et <i>al.,</i> 2009 (37)
	Flame structure	T_{fg} =300 K ; P=30 Torr ; Φ =1.75 Only mass spectrum provided	Li et <i>al.,</i> 2010 (38)
		T _{fg} =300 K ; P=30 Torr ; Φ=0.75-1.75	Li et <i>al.,</i> 2011 (39)
		T _{fg} =298 K ; P=36 Torr ; Φ=0.7, 1	Detilleux et <i>al.,</i> 2011 (40)





In 2002, Dagaut et *al.* (16) were the first to study the oxidation of toluene in a jet-stirred reactor at high temperatures (1000-1375 K) and equivalence ratios of 0.5 and 1 to perform species concentration measurements with GC analysis. After that, Bounaceur et *al.* (17) studied the jet stirred reactor oxidation of toluene at 1 atm, between 873 and 923 K and equivalence ratios from 0.45 to 0.91. Yuan et *al.* (10) reported data on toluene oxidation in a JSR at pressure of 10 atm, residence time of 0.6 *s*, equivalence ratios of 0.5, 1.0 and 1.5, and temperatures from 950 to 1200 K and proposed the most recent model on toluene oxidation, which includes 272 species and 1698 reactions. The most common major products detected in these JSR studies were CO, CO_2 , acetylene, phenol, benzene, ethylbenzene, and styrene.

Concerning flame structures, Detilleux et *al*. (37,40) published results on a rich toluene flame in 2009 and on lean and stoichiometric flames in 2011. Both measurements were achieved at low pressure (36 Torr) on a flat flame burner. Data under rich condition give information about the formation of the largest aromatics. The pathways yielding C_7H_6 , determined theoretically, were validated thanks to identification and quantification of C_7H_6 and C_7H_7 . Globally, these whole results highlight three decomposition pathways of toluene, all ending with cyclopentadienyl radical formation.

Li et *al.* (36,38) measured species profiles in a rich flames (Φ =1.75, 1.9) under low pressure (30 Torr) thanks to a flat flame burner coupled to SVUV-PIMS. Li *al.* (39) conducted two years later a similar study under a wider range of equivalence ratio (0.75, 1, 1.25, 1.5 and 1.75). These works highlighted the importance of benzyl radical in toluene chemistry and upgraded knowledge about the formation of Polycyclic Aromatic Hydrocarbons (PAH). Major detected intermediates are the same ones in these four studies: acetylene is formed in the largest amounts whatever the conditions, followed by methane and benzene.

First toluene LBV measurements were performed in 1996 by Davis et *al.* (18) with a Counter Flow burner (CF) under atmospheric conditions. Data were obtained under same conditions, with the same kind of facility by Davis et *al.* (19) in 1998 and Hirasawa et *al.* (20). The CF burner was the most used apparatus for investigating toluene flame with more data published, under atmospheric pressure, by Kumar et *al.* (21) (Tfg =400, 470 K), Ji et *al.* (22,23) (Tfg =353, 403 K), Hui et *al.* (24) (Tfg =400, 470 K); in another paper, Hui et *al.* (25) showed results under 1, 2 and 3 atm (Tfg =400 K).

Other measurements were performed in a Constant Volume Chamber (CVC) under 1 atm by Zhang et *al.* (29) (Tfg =393, 433 K), by Wang et *al.* (27) (Tfg =358, 423 K) who increased pressure until 20 atm, and by Zhong et *al.* (28) (Tfg =400, 450 K) with additional experiments under 3 atm. A similar facility has been developed by Han et *al.* (30) to perform measurements under constant pressure, from 1 to 5 atm.

Bunsen burners coupled with chemiluminescence technics were used under atmospheric pressure by Munzar et al. (31) (Tfg =400 K) and Wu et al. (Tfg =423 K) (32).

Finally, data were obtained on a flat flame burner using the heat flux method under atmospheric pressure by Sileghem et *al.* (Tfg =298, 358 K) (33), Dirrenberger et *al.* (Tfg =298, 358, 398 K) (34) and Liao et *al.* (35) (Tfg =298). It is noticeable that most of these experiments were completed under fresh gas temperature of 298K, around 358 K and 398 K what allows comparison of data. A belt shape, centred at Φ =1.1 is observed. Under atmospheric pressure, top values are about 45cm/s for fresh gas around 358 K and about 55 cm/s for fresh gas around 398 K (see Figure 1). The figure 1 shows existing data for T_{fg} around 398 K and highlights the sparsity of results with deviations often higher than 10 cm/s. Comparing various kind of facilities, the flat flame burner presents an excellent repeatability with very close results between studies.





Figure 1. Toluene laminar Burning Velocities under atmospheric pressure for fresh gas around 398 K.

1.2. Styrene

There have been fewer experimental studies on the combustion of styrene as shown in Table 4. The first kinetic experiments were made by Litzinger et *al.* in 1896 (41) and concerned its oxidation in an atmospheric flow reactor at temperatures around 1060 K. The main stable products detected were CO, methane, ethane, benzene, phenol and cyclopentadiene. After that, Grela et *al.* (42) were the first to study the unimolecular decomposition of styrene. The experiments were carried out at very low pressure between 1180 and 1350 K. In 2001, Comandini et *al.* (43) investigated the ignition delay times of styrene in a shock tube at the pressures of 1.43 atm and temperatures of 1300-2000 K.

Concerning JSR study, there is not data for neat styrene as reactant. However, Yuan et *al*. (44) investigated the oxidation of a styrene/benzene mixture at three equivalences ratios (Φ = 0.5, 1 and 1.5), at 10 atm and over the temperature range of 1000-1357 K. The main stable products detected were small hydrocarbons (methane, ethane, and ethylene), with also benzene, phenol, and benzaldehyde. A detailed chemical kinetic model of the combustion of styrene including 290 species and 1786 reactions was established and validated.

In 2016, LBV of styrene were measured by Meng et *al*. (45) and Comandini et *al*. (43) both using the bomb method under 1 bar. These data were established for fresh gas temperatures from 342 K to 450 K and the top value, for Φ =1.1, is close to 65 cm/s for fresh gas at 398 K.

Li et *al.* (38) performed species measurements on a rich styrene flame using a flat flame burner but only mass spectra were provided. In 2015, Yuan et *al.* (44) studied the structure of styrene flames using a flat flame burner under low pressure (3.95 kPa) for various equivalence ratios (Φ =0.75, 1, 1.7). Measurements were performed with SVUV-PIMS highlighting both the tendency to produce soot and the dominant consumption pathways by O-, H- atoms and OH attack reactions. Acetylene was the main intermediate followed by benzaldehyde under poor conditions and ethylene under rich conditions; benzene was also detected in large amount whatever the equivalence ratio.



Table 4: Main	experimental studi	es about styrene	gas-phase reactions
rable in main	experimental staal	es about styrene	Bus phase reactions

Instrument	Measured property	Experimental Conditions	Reference
	Species profiles	T=1060 K; Φ=0.56; P=1 atm	Litzinger et <i>al.,</i> (1986) (41)
Flow reactor		T=1180-1350 K; P=0.000013 atm; Φ=∞	Grela et <i>al.,</i> (1992) (42)
Shock tube	Ignition delay times	T=1300-2000 K; P=1.43 atm	Comandini et <i>al.,</i> 2016 (43)
Constant Volume	Laminar burning velocity	T _{fg} =398, 450 K ; P=1 bar ; Φ=0.8-1.5	Meng et <i>al.,</i> (2016) (46)
Chamber		T_{fg} =342-405 K ; P=1 bar ; Φ =0.75-1.45	Comandini et <i>al.,</i> 2016 (43)
Flat flame burner	Flame structure	T _{fg} =300 K; P=0.039 atm; Φ=1.7 Only mass spectrum provided	Li et <i>al.,</i> 2010 (38)
		T _{fg} =300 K ; Φ=0.75-1.7; P=0.029 atm.	Yuan et <i>al.,</i> 2015 (44)

1.3. Xylene isomers

The very first study about xylene isomers was reported by Barnard and Sankey in 1968 (47,48), who investigated the oxidation of the three xylene isomers in the temperature range 733 to 785 K in a conventional static reactor. They observed that *ortho*-xylene possessed a much greater degree of reactivity towards oxygen than its isomers *meta*- and *para*-xylene. Following this first work, as shown in Tables 5 and 6, xylene combustion has been investigated extensively. Emdee *et al.* (49,50) investigated the oxidation of the three isomers in an atmospheric flow reactor at temperatures between 1093 and 1199 K. Using GC, they detected xylylene and recommended it as the source of the higher reactivity of o-xylene due to its fast isomerization to styrene. More recently, the pyrolysis *ortho*-xylene was studied by Yuan *et al.* (51) using a flow reactor at pressures 0.04-1 atm and temperatures 1050-1600 K, confirming the presence of xylene through SVUV-PIMS analysis.

The oxidation of the three xylene isomers was studied in a jet-stirred reactor by Gail *et al.* (52–54) between 900 and 1400 K, at 10 bar. The highest reactivity was observed for *ortho*-xylene and products quantified by GC included CO, CO₂, CH₂O, CH₄, C₂H₂, C₂H₄, C₂H₆, allene, propyne, C₃H₆, acrolein, 1,3-C₄H₆, vinylacetylene, 1,3-cyclopentadiene, benzaldehyde (as shown in figure 2). A detailed kinetic model was proposed for each isomer. In 2021, this work was completed by a study made at 10 bar between 800 and 1200 K for *ortho*-xylene by Yuan *et al.* (51), who proposed a detailed model based on their previous ones for aromatic compounds and consisting of 415 species and 2726 reactions. No JSR measurement below 800 K is available, not even for *ortho*-xylene for which low temperature reactivity might be expected.





Figure 2: Oxidation of *ortho*-xylene in a JSR at 1 atm and Φ = 0.5. The initial conditions were 0.10% fuel 2.10% O₂, 97.80% N₂ in mole; τ = 0.1 s. Experimental data (symbols) are compared to computations (lines and small symbols) (54).

In 2000, Roubaud et *al.* (55,56) used a rapid compression machine to measure the auto-ignition delay times of a series of arenes, including xylene isomers, in the temperature region 600-900 K, at compressed pressures up to 25 bar. They observed that toluene, *meta*-xylene, *para*-xylene, and *1,3,5*-trimethylbenzene ignited only above 900 K and 16 atm, while *ortho*-xylene, *1,2,3*-trimethylbenzene and *1,2,4*-trimethylbenzene ignited at much lower temperatures and pressures. They concluded that the addition of molecular oxygen to benzylic-type radicals leads to low temperature branching increasing the reactivity only when the transfer of hydrogen in the isomerization step occurs from an ortho-alkyl group. In 2019, also using a rapid compression machine, Kukkadapu et *al.* (57) measured ignition delay times of *ortho*-xylene between 833 and 1000 K under pressures from 25 to 45 atm and proposed a detailed kinetic





model for methylated aromatics, including toluene, *ortho*-xylene, *para*-xylene, *1,2,4*-trimethylbenzene, *1,3,5*-trimethylbenzene.

Concerning shock tube ignition, Battin-Leclerc et *al.* (58) measured ignition delay times for all three xylene isomers at 1330-1800 K and pressures from 6.7 to 9 bar. These last authors observed no discernible difference in the reactivity of the three isomers under their conditions, and they developed a comprehensive kinetic oxidation mechanism for all three xylene isomers. After that, Shen and Oehlschlaeger (59) carried out similar measurements at somewhat lower temperatures (941-1408 K) and pressures ranging from 9 to 45 atm. It was shown that *ortho*-xylene was slightly more reactive than *para*- and *meta*-xylene, and the ignition delay times of *para*- and *meta*-xylene were similar to those of toluene under comparable conditions. Gudiyella et *al.* (60) studied the oxidation of *meta*-xylene in a single pulse shock tube between 1024 to 1650 K, at high pressures (P=20-50 atm) and quantified using GC the formation of a variety of stable species ranging from small hydrocarbons, to single ring and PAH (e.g. naphthalene, anthracene and acenaphthylene).

Xylene flame structures were first studied by Li et *al.* (38) in 2010 with a flat flame burner equipped with molecular-beam sampling system and SVUV-PIMS analysis. Measurements were performed with the three xylenes under rich condition (Φ =1.79) allowing the identification of PAH until C₁₉ species. With the same apparatus, Zhao et *al.* (61) studied flames of *ortho*-xylene and Yuan et *al.* (62) of *para*-xylene, both with lean, stoichiometric and rich mixtures (Φ =0.75, 1, 1.79). Over 30 species were identified; the main quantified intermediates being, in both studies, acetylene, benzene, ethylene, toluene and, under poor conditions, aldehydes. Li et *al.* (38) and Zhao et *al.* (61) highlighted the key role of benzyl and phenyl radicals in the PAH formation and Zhao et *al.* (61) proposed another pathway for the formation of indene and naphthalene starting from *ortho*-xylene thanks to reactions of *ortho*-xylyl radical. For these first PAHs, Yuan et al. (62) proposed a pathway from *para*-xylene by via xylylene and styrene in rich flame.

Concerning laminar burning velocities (LBV), measurements were completed by Johnston et *al.* (26) for *meta*-xylene using the bomb method for fresh gas at 450 K and 3 atm. Using a counter flow burner, Ji et *al.* (23) measured LBV with the three xylene isomers under atmospheric pressure and for a fresh gas temperature of 353 K. Han et *al.* (30) obtained data for *ortho*-xylene from 1 to 2 atm in a chamber under constant pressure. Finally, concerning LBV measurements using a flat flame burner, only *para*-xylene was considered, by Dupont et *al.* (63) who worked under atmospheric pressure for fresh temperature from 328 to 353 K. It seems that the three isomers have the same LBV with the maximum value, between 40 and 45 cm/s under 1 atm around 358 K, reached close to Φ =1.1.





Table 5: Main experimental studies about the gas-phase reactions of xylenes not involving flame.

Instrument	Measured property	Studied isomers	Experimental Conditions	Reference
Flow reactor		0-	T = 1150 K ;Φ = 0.69,1.1,1.7; P =1 atm.	Emdee et <i>al.,</i> 1991 (49)
		m-, p-	T = 1093-1199 K ;Φ = 0.47-1.7, 1; P = 1 atm.	Emdee et <i>al.,</i> 1991 (50)
		0-	T = 1050-1625 K ;Φ = ∞; P = 0.04, 1 atm.	Yuan et <i>al.,</i> 2021 (51)
	Species profiles	p-	T = 900-1300 K; Φ = 0.5-1.5; t=0.1 s; P = 1 atm.	Gail et <i>al.,</i> (52)
Jet-stirred		m-	T = 900-1400 K; Φ = 0.5-1.5; t=0.1 s; P = 1 atm.	Gail et <i>al.,</i> (53)
reactor		0-	T = 900-1400 K; Φ = 0.5-1.5; t=0.1 s; P = 1 atm.	Gail et <i>al.,</i> (54)
		0-	T = 800-1200 K; Φ = 0.5-2; t=0.5 s; P = 10 atm.	Yuan et <i>al.,</i> 2021 (51)
Rapid	Ignition delay times	o-, m-, p-	T = 600-900 K ; P < 24.6 atm.	Roubaud et <i>al.,</i> (55,56)
machine		0-	T= 830-980 K; Φ = 0.5, 1 ; P=25, 45 bar	Kukkadapu et <i>al.,</i> (57)
Shock tube		o-, m-, p-	T = 1330-1800 K; Φ = 0.5-2; P = 5.9-8.8 atm.	Battin-Leclerc et <i>al.,</i> (58)
		o-, m-, p-	T = 941-1408 K; Φ = 1.0,0.5; P = 9-45 atm.	Shen et <i>al.,</i> 2009 (59)
		m-	T = 1024-1632 K; Φ = 0.53,1,2.35; P = 25-50 atm.	Gudiyella et <i>al.,</i> (60)



Instrument	Measured property	Studied isomers	Experimental Conditions	Reference
Constant Volume Chamber	Laminar burning velocity Flame structure	m-	T _{fg} =450 K ; P=3 atm ; Φ=0.8-1.4	Johnston et <i>al.,</i> 2005 (26)
Constant Pressure Chamber		0-	T _{fg} =353 K ; P=1-2 atm ; Φ=0.7- 1.5	Han et <i>al.,</i> 2017 (30)
Counter Flow burner		o-, m-, p-	T_{fg} =353 K ; P=1 atm ; Φ =0.7-1.5	Ji et <i>al.,</i> 2012 (23)
		p-	T _{fg} =328-353 K ; P=1 atm ; Φ=0.7- 1.4	Dupont et <i>al.,</i> 2019 (63)
Flat flame burner		o-, m-, p-	T _{fg} =330 K ; P=4 kPa ; Φ=1.79 Only mass spectrum provided	Li et <i>al.,</i> 2010 (38)
		0-	T _{fg} = 300K ; P=4 kPa ; Φ=0.75, 1, 1.79	Zhao et <i>al.,</i> 2015 (61)
		p-	T _{fg} = 300K ; P=4 kPa ; Φ=0.75, 1, 1.79	Yuan et <i>al.,</i> 2021 (62)

Table 6: Main experimental kinetic studies about xylene flames. T_{fg} is the temperature of fresh gas.



1.4. Ethylbenzene

As is shown in Table 7, the first studies about the oxidation of ethylbenzene are due to team of Brezinsky in an atmospheric flow reactor. In 1982, Venkat *et al.* (64) worked at a temperature close to 1200 and in 1986, Litzinger *et al.* (41) at a temperature close to 1060 K. CO, CO₂, CH₂O, CH₄, C₂H₂, allene, vinylacetylene and benzaldehyde were the major products detected and quantified in both studies (41,64).

Roubaud *et al.* (55) used a rapid compression machine to measure the auto-ignition delay times in the temperature region 600-900 K, at compressed pressures up to 25 bar. Shen et Oehlschlaeger (59) investigated the ignition delay times of ethylbenzene in a shock tube at the pressures of 9 to 45 atm over a range temperature from 941 to 1408 K.

Husson *et al.* (65) investigated the oxidation of ethylbenzene in a jet stirred reactor at 1 atm, between 750 and 1100 K. The major products detected using on-line GC were CO, CO₂, methane, acetylene, phenol, benzene, ethylbenzene, and styrene. Yuan *et al.* (66) used a flow reactor and a jet stirred reactor to study the pyrolysis and the oxidation of ethylbenzene, respectively. The experiments were performed over a temperature of 850-1500 K for pyrolysis and 800-1400 K for oxidation, at various pressures (P=0.04, 0.2 and 1 atm). A detailed kinetic model of the combustion of ethylbenzene including 229 species and 1563 reactions was developed by extending their publishing toluene (10,11) and styrene (44) models. They concluded that styrene and benzyl radical were the key intermediates in ethylbenzene consumption and PAHs formation. The more recent work on the oxidation of ethylbenzene was performed by Herbinet *et al.* (67) in a jet stirred reactor at pressures up to 10 atm and at temperatures from 500 to 1100 K. The main products obtained were CO, acetylene, CO₂, phenol, benzene, and styrene; minor products were methane, ethane, propyne, propadiene, and propylene.

Most of the LBV were measured with the bomb method in a CVC beginning by Johnston *et al.* (26) who performed experiments under 3 atm for a fresh gas temperature of 450 K. Meng *et al.* (45) achieved measurements for fresh gas at 358, 398 and 450 K under atmospheric pressure. Wang *et al.* (27) obtained data from 1 to 10 atm for T_{fg} =423 K. Finally, Mehl *et al.* (68) used an atmospheric flat flame burner to measure LBV for fresh gas at 358 and 398 K. Under atmospheric pressure, top values, reached around Φ =1.1, are close to 50 cm/s for fresh gas at 358 K and almost attain 60 cm/s for fresh gas at 398 K.

Ergut *et al.* (69–71) used a flat flame burner under atmospheric pressure to measure species profiles in rich flames for equivalence ratios above 1.68. These experimental studies, complemented with a numerical work, focused on ethylbenzene decomposition and PAH formation. According to these studies, acetylene, the major intermediates, is directly linked to soot formation. Using the same kind of facility under low pressure (0.04 atm), Li *et al.* (38,72,73) investigated the chemistry of ethylbenzene under lean, stoichiometric, and rich conditions. In accordance with Li *et al.* (38,72,73) results, acetylene is the main intermediates under rich conditions and is directly linked to the PAH formation through the H-abstraction / C_2H_2 -addition. Whatever the equivalence ratio, benzene and ethylene are the following major intermediates; methane is detected in low quantity while it is one of the main intermediates in atmospheric flames.



Table 7: Main experimental studies about ethylbenzene gas-phase reactions.

Instrument	Measured property	Experimental Conditions	Reference
	Species profiles	T=1200 K; Φ=0.79; P=1 atm	Venkat et <i>al.,</i> 1982 (64)
Flow reactor		T=1060 K; Φ=0.64, 0.95 and 1.3; P=1 atm	Litzinger et <i>al.,</i> 1986 (41)
		T=850-1500 K; Φ=∞ ; P=0.04,0.2 and 1 atm.	Yuan et al., 2016 (66)
RCM	Ignition delay times	Т=600–900 К; Ф=1; Р=9-45 atm.	Roubaud et <i>al.,</i> 2000 (55)
		T=750-1100 K; P=1 atm; Φ=0.25, 1 and 2	Husson et <i>al.,</i> 2012 (65)
Jet-stirred reactor	Species profiles	T=1000-1400 K; T=800-1280 K; P=1 and 10 atm; Φ=0.5, 1 and 1.5	Yuan et al., 2016 (66)
		T=500-1100 K; P=1-10 atm; Φ=0.25, 1 and 2	Herbinet et <i>al.,</i> 2020 (67)
Shock tube	Ignition delay times	T=941-1408 K; P=9-45 atm, Φ=0.5-1	Shen and Oehlschlaeger 2009 (59)
Constant Volume Chamber		Т _{fg} =450 К ; Р=3 atm ; Ф=0.8-1.4	Johnston et <i>al.,</i> 2005 (26)
		Т _{fg} =358-450 К ; Р=1 atm ; Ф=0.8-1.5	Meng et <i>al.,</i> 2016 (45)
		T _{fg} =423 K ; P=1-20 atm ; Φ=0.6-1.5	Wang et <i>al.,</i> 2017 (27)
		T _{fg} =358-398 K ; P=1 atm ; Φ=0.55-1.6	Mehl et <i>al.,</i> 2015 (68)
	_	T _{fg} =298 K ; P=1 atm ; Φ=2.5	Ergut et <i>al.,</i> 2006 (69)
Flat flame burner	Flame structure	T _{fg} =298 K ; P=1 atm ; Φ=1.68, 1.74, 1.83	Ergut et <i>al.,</i> 2007 (70), Ergut et <i>al.,</i> 2009 (71)
		T _{fg} =273 K ; P=0.04 atm ; Φ=1.9	Li et <i>al.,</i> 2009 (72)
		T _{fg} =300 K ; P=0.3 atm ; Φ=1.79	Li et <i>al.,</i> 2010 (38)
		T _{fg} = 300K ; P=0.04 atm ; Φ=0.75, 1, 1.79	Li et <i>al.,</i> 2011 (73)



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The main experimental studies about the pyrolysis, oxidation and flames of neat *n*-propylbenzene are listed in Table 8. The *n*-propylbenzene ignition delay times was measured first using a rapid compression machine by Roubaud et *al*. (55) for temperatures from 600 to 900 K, around a pressure of 25 atm. They observed that alkylbenzenes, such as *n*-propyl- and *n*-butylbenzenes, presented features of low-temperature reactivity with the occurrence of a two-stage ignition. After that, Darcy et *al*. (74–76) measured again the ignition delay times using a rapid compression machine at 800-1600 K, pressures from 1 to 50 atm.

Gudiyella and Brezinsky (77,78) investigated the pyrolysis and the oxidation of *n*-propylbenzene in a singlepulse shock tube at temperatures between 838-1669 K for pyrolysis and 1027-1678 K for oxidation. Using GC, they detected CO, CO₂, CH₄, benzene, toluene, styrene, phenol and benzaldehyde.

Concerning jet stirred reactor oxidation, Dagaut et *al*. (79) preformed experiments for *n*-propylbenzene at high temperature (T=900-1250 K), at atmospheric pressure and measured species concentration by GC. CO, CO₂, CH₄, benzene and styrene were the main products identified.

Yuan et *al.* (80) investigated a combustion of *n*-propylbenzene using a flow reactor for pyrolysis and a jet stirred reactor for oxidation. The pyrolysis experiments were carried out over a temperature range of 750-1400 K, at pressures of 0.04, 0.2 and 1 atm, the oxidation experiments were performed at 10 atm, at temperature from 750 to 1200 K. Based on their results, they developed a model containing 340 species and 2069 reactions. The main stable products detected under both conditions were CO, CO_2 , methane, ethane, benzene, toluene and styrene. Another study has been performed in a JSR by Liu et *al.* (81) on the oxidation of *n*-propylbenzene in the temperature range of 700-1100 K, at pressures of 1, 3 and 6 atm. The main major products detected were CO, methane, benzene, toluene and styrene.

Johnston et *al.* (26) and Kim et *al.* (82) used a constant volume chamber to measure LBV under atmospheric pressure (T_{fg} =353, 400 K) and 3 atm (T_{fg} =450 K). As with other arenes, Ji et *al.* (23) and Hui et *al.* (24,25) measured LBV with a counter flow burner. Ji et *al.* (23) worked with a fresh gas temperature of 353 K under atmospheric pressure while Hui et *al.* (24,25) obtained data from 1 to 3 atm. Mehl et *al.* (68) performed measurements with a flat flame burner using the heat flux method under 1 atm for fresh gas at 358 and 398 K. Finally, in 2018, Wu et *al.* (83) and Liu et *al.* (81) achieved experiments with a Bunsen burner. Wu et *al.* (83) worked under atmospheric pressure and fresh gas at 473 K. In each case, maxima are reached around an equivalence ratio of 1.1; the LBV almost attains 50 cm/s for fresh gas around 358 K, and is about 60 cm/s for fresh gas around 398 K.

Concerning flame structures, Wang et *al*. (84) studied *n*-propylbenzene kinetic under rich conditions (Φ =1.79) and Yuan et *al*. (80) under lean and stoichiometric conditions (Φ =0.75, 1) using a low-pressure flat flame burner. The main quantified intermediates were acetylene and ethylene, due to alkyl chain in the molecule of *n*-propylbenzene; significant amount of indene and styrene was formed compared to flame studies with other aromatics. Whatever the condition, the benzylic C-C bond dissociation is a key pathway of *n*-propylbenzene decomposition in rich flames.





Table 8: Main experimental studies about *n*-propylbenzene gas-phase reactions (neat fuel).

Instrument	Measured property	Experimental Conditions	Reference	
RCM	Ignition dolog	T=600-900 K; Φ=1; P <25 atm	Roubaud et <i>al.,</i> 2000 (85)	
	times	T=650-1000 K, Φ= 0.29, 0.49, 0.96 and 1.92; P=10, 30 and 50 atm.	Darcy et <i>al.,</i> 2014 (75)	
		T=900-1250 K; P=1 atm; Φ=0.5 and 1.5	Dagaut et <i>al.,</i> 2002 (79)	
Jet-stirred reactor		T=700-1100 K; P=1, 3 and 6 atm; Φ= 0.4 and 2	Liu et <i>al.,</i> 2018 (81)	
	Species profiles	T=750-1200 K; P=10 atm; Φ= 0.5, 1,1.5 and 2	Yuan et <i>al.,</i> 2017 (80)	
Shook tubo		T=838-1669K ;P=25 and 50 atm; Φ= 0.5–1.9	Gudiyella and Brezinsky et <i>al.,</i> 2012 (77)	
Shock tube		T=1027-1678K ;P=50 atm; Φ= ∞	Gudiyella and Brezinsky et <i>al.,</i> 2013 (78)	
Flow reactor		T=750-1400 K;P=0.04, 0.2 and 1 atm; Φ = ∞	Yuan et <i>al.,</i> 2017 (80)	
Constant Volume		T_{fg} =450 K ; P=3 atm ; Φ =0.8-1.4	Johnston et <i>al.,</i> 2005 (26)	
Chamber		T _{fg} =353, 400 K ; P=1 atm ; Φ=0.7-1.5	Kim et <i>al.,</i> 2012 (82)	
Bunsen burner		T _{fg} =400 - 473 K ; P=1 atm ; Φ=0.65-1.3	Wu et <i>al.,</i> 2018 (83)	
	Laminar burning velocity	T _{fg} =473 K ; P=1-6 atm ; Φ=0.6-2	Liu et <i>al.,</i> 2018 (81)	
		T _{fg} =353 K ; P=1 atm ; Φ=0.7-1.5	Ji et <i>al.,</i> 2012 (23)	
Counter Flow burner		T _{fg} = 400, 470 K ; P=1 atm ; Φ=0.7-1.4	Hui et <i>al.,</i> 2012 (24)	
		T _{fg} = 400 K ; P=1-3 atm ; Φ=0.7-1.4	Hui et <i>al.,</i> 2013 (25)	
		T _{fg} = 358-398 K ; P=1 atm ; Φ=0.55-1.35	Mehl et <i>al.,</i> 2015 (68)	
Flat flame burner	Flame structure	T _{fg} =300 K ; P=0.04 atm ; Φ=1.79	Wang et <i>al.,</i> 2013 (84)	
		T _{fg} =300 K ; P=0.04 atm ; Φ=0.75, 1	Yuan et <i>al.,</i> 2017 (80)	



1.6. Trimethylbenzene isomers

Trimethylbenzenes are important alkyl aromatics detected in the diesel and aviation fuels, whose combustion kinetics have been further studied in recent years. Table 9 presents the main experimental studies about 1,3,5-trimethylbenzene (mesitylene or T135MB) and 1,2,4-trimethylbenzene (T124MB) combustion that were found in literature. Roubaud et *al.* (55) were the first to measure the auto-ignition features of T135MB and T124MB in a rapid compression machine, for temperatures and pressures after compression between 600 and 900 K and 5 and 25 atm, respectively. Diévart et *al.* (86) used a shock tube to measure the ignition delay times of T135MB at temperatures from 1111 to 1468 K, at 9.8 and 21.7 atm. An estimated kinetic model was proposed to predict the species profiles. One year later, Rao et *al.* (87) measured the ignition delay times of T135MB at pressures of 1, 5, and 20 atm in a heated shock tube over the temperatures of 1080–1560 K. Very recently, Liang et *al.* (88) performed a comparative experimental and kinetic modelling study of the high-temperature ignition of *n*-propylbenzene, T135MB, and T124MB. The studied pressure was 2, 5 and 10 bar and the temperature range was from 1090 to 1600 K. *n*-Propylbenzene was found as the most reactive.

In 2012, Gudiyella et and Brezinsky (89) investigated the oxidation of 135MB in their single-pulse shock tube, for pressures between 20 and 55 atm, and a temperature range of 1017-1645 K. They quantified a wide range of species from aliphatic hydrocarbons to single ring and PAH

Concerning trimethylbenzenes oxidation studies performed in a jet stirred reactor, in 2016, Weng et *al.* (90) studied the oxidation of T124MB over the temperature range of 700-1100 K, at atmospheric pressure. A large variety of products was identified using on-line GC including benzene, toluene, ethylbenzene, *orthopara-* and *meta-*xylene. Two years later, Wang et *al.* (91) investigated the oxidation of neat T135MB under the same pressure/temperature conditions. Using online GC, they identified and quantified as the major products CO₂, benzene, styrene, toluene, and benzaldehyde. The same team (92) studied the oxidation of *n*-decane/T135MB mixture, over the temperature range of 500-1100 K at atmospheric pressure. During this latter study, they showed that the presence of T135MB has a somewhat inhibiting effect on the oxidation of n-decane. Additionally, the formation of aromatics is partially inhibited by the addition of n-decane, resulting in lower peak concentrations at low temperatures compared to pure T135MB. Liu et *al.* (93) reported a comparison study of the oxidation of T135MB,T124MB, *n*-propylbenzene and *iso*-propylbenzene in the same JSR under the same experimental conditions (T= 700 to 1100 k, P=1 atm), showing that *iso*-propylbenzene is the most reactive fuel and T135MB the least one.

In 2012, Ji et *al.* (23) and Hui et *al.* (24) both measured LBV of T124MB and T135MB using a counter flow burner. They achieved measurements under atmospheric pressure for fresh gas temperature of 353 K (23), 400 and 470 K (24). Later, Hui et *al.* (25) published data under higher pressures, until 3 atm, for T124MB. In 2013, Diévart et *al.* (86) measured LBV of T135MB using the bomb method under the same conditions as Hui et *al.* (24) in 2012 (1 atm, 400 K). According to these results, it seems that these two studied isomers have the same LBV. The top of the belt profile is around Φ =1.1; under 1 atm it almost reaches 40 cm/s for fresh gas around 358 K, and about 50 cm/s for fresh gas around 398 K.





Instrument	Measured property	Studied isomers	Experimental Conditions	References	
RCM	lgnition delay	1.2.4 and 1.3.5	T= 600-900 K; P= 5-25 atm; Φ= 1	Roubaud et al., 2000 (55)	
	lgnition delay	1.3.5	T= 1111-1468 K; P= 9.8 and 21.7 atm; Φ=0.5,1.0 and 2	Diévart et <i>al.,</i> 2013 (86)	
			T= 1080-1560 K; P= 1.0, 20 atm; Φ= 0.5,1 and 2	Rao et <i>al.,</i> 2014 (87)	
Shock tube	Species profiles		T= 1017-1645 K; P= 20, 50 atm; Φ = 0.5,1.0 and 1.9	Gudiyella et and Brezinsky, (2012) (89)	
	lgnition delay	1.3.5	T= 1280-1550 K; P= 2, 5 and 10 atm; Φ= 0.5,1 and 2	Liang et al.,(2022) (88)	
		1.2.4	T= 1140-1600 K; P= 5 bar; Φ = 0.5,1 and 2	Liang et al.,(2022) (88)	
		1.2.4	T= 700-1100 K; P= 1 atm; Φ=2	Weng et <i>al.,</i> (2016) (90)	
Jet-stirred reactor	Species profiles	1.3.5	T= 700-1100 K; P= 1 atm; Φ= 0.4-1.0	Wang et <i>al.,</i> (2018) (91)	
		1.2.4 and 1.3.5	T= 700-1100 K; P= 1 atm; Φ = 2	Liu et <i>al.,</i> 2019 (93)	
		1.2.4 and 1.3.5	T _{fg} =353 K ; P=1 atm ; Φ=0.7-1.5	Ji et <i>al.,</i> 2012 (23)	
Counter flow burner	Laminar	1.2.4 and 1.3.5	T _{fg} =400, 470 K ; P=1 atm ; Φ=0.7-1.4	Hui et <i>al.,</i> 2012 (24)	
	burning velocity	1.2.4	T_{fg} =400 K ; P=1-3 atm ; Φ =0.7-1.4	Hui et <i>al.,</i> 2013 (25)	
Constant Volume Chamber		1.3.5	T _{fg} =400 K ; P=1 atm ; Φ=0.7-1.5	Diévart et <i>al.,</i> 2013 (86)	



2.Analysis of the samples provides by Vertoro and Aalto.

The compositions of the bio-oils sent by Vertoro in November 2021 and by Aalto in May 2022 were determined using a GC-MS-FID setup and a GCxGC-MS-FID one. The MS was used for the identification of the species. The FID was used for the quantification of the species. The samples sent by Vertoro and Aalto contained some solid black particles, thus the solutions were filtered before being analysed. Given the high dilution into solvent (methanol for Vertoro, ethanol for Aalto), a low spilt ratio of 1:10 was used for the analysis using the GC-MS-FID setup. The procedure for obtaining the bio-oil provided by Vertoro was described in detail in the deliverable 4.2, entitled "Bench scale EHL samples for the investigations (set 2 batches)" and released in October 2021. The procedure used in Aalto will be provided in a future deliverable.

2.1. Analytical procedure for bio-oil analysis.

The first apparatus used is a gas chromatograph provided by Agilent (7890A) with a 7000A triple quadrupole mass spectrometer (used as a simple quadrupole here). The injection was performed using an automatic liquid sampler (ALS) with an injection volume of 1 µL. The injector was used with the split mode with a split ratio of 1:10. It was heated at 250°C. The column used for the separation was an HP5 column (Agilent 19091S-433A) with the following properties: 30m × 250µm × 0.25µm. The carrier gas was helium. Constant flow mode was selected, and the helium flow rate in the column was 1.5 mL/min. The oven temperature profile was 30°C for 4.3333 min, then 6°C/min to 250 °C for 39 min. The end of the column was connected to a splitter with auxiliary helium flow maintaining the pressure at 1 psi. The flow was then divided in two parts for analysis with the flame ionization detector (FID) and the mass spectrometer. Fused silica restrictions were used to divide the flow in two parts with similar flow rates towards the two detectors. The FID was heated at 300°C. Air, hydrogen and makeup helium flow rates were, 400, 45 and 30 mL/min, respectively. The transfer line to the mass spectrometer was heated at 280°C. The analysis could seem long, but the goal was to obtain a good peak separation. For the quantification, an internal standard (n-octane) was added to the mixture. Then the masses of species in the mixture were calculated from that of *n*-octane. The relationship between calibration factors of a given species and *n*-octane were obtained using the Effective Carbon Number method (94), which relies on the contribution of carbon atoms to the overall response of a species.

Analyses were also performed using two-dimensional gas chromatography working under similar conditions as those used for the GC-MS-FID analyses. An Agilent 7890A equipped with an Agilent 7683B autosampler and FID was coupled to an Agilent 5975C inert MSD with triple-axis detector. Cryogenic modulation was performed using a ZOEX ZX1 loop modulator. Injection was made at 200°C with a 0,2µL injection volume. The first column consisted of a Restek Rxi-5Sil MS 13639 (30m x 320µm x 0.5µm). The first column flow rate was 1.5ml/min under constant flow condition. The modulation time was 4s with a 0.4s hot jet pulse. The second column was an Agilent HP-Innowax 19091N-133I (1.4m x 250µm x 0.25µm). The oven program was 30°C – 6°C/min – 250°C (10min), for a total run time of 46.67 min. The second column was exposed to an auxiliary oven fixed at 200°C. The second column was connected to a splitter, allowing for simultaneous collection of data from both the FID and MS. MS inferior detection limit was set at 45 m/z to avoid detection of residual water, air and carbon dioxide. Modulation was performed using SRA Instruments Optimode V2.0. Instrumental control and data collection were performed using Agilent



ChemStation. Data processing was performed using GCImage. For qualitative identification, NIST 17 v2.3 was used.

2.2. Analysis of the sample provided by Vertoro

The species present in the bio-oil provided by Vertoro have been identified using the procedure described above. The FID signal was used for the quantification and the determination of the mass composition.

2.2.1. Mass composition of the Vertoro bio-oil.

Figure 1 shows the mass composition (in %) of the bio-oil provided by Vertoro. The solvent (methanol) was not considered in the calculation because the mixture is highly diluted and mass fractions would be insignificant and meaningless (it is planned to recycle the solvent in the practical application). Most of species present in the mixture are phenolic compounds as expected from the lignin structure.



Figure 1 - Composition of the Vertoro bio-oil (solvent taken apart).

The main species are 2,2-dimethoxypropane, 2-methoxy,4-popylphenol, anisole, p-cresol and guaiacol. The presence of 2,2-dimethoxypropane was not expected from the decomposition of the lignin. This species may come from the process. Also, low concentrations of methyl stearate and oleate have been measured. These species likely come from impurities (triglycerides) present in the feedstock. The mixture also contains some *n*-dodecane, which is an internal standard used by Vertoro (as explained in D4.2).



There is a doubt about the identification of 3,5-dimethoxy-benzaldehyde. The global formula is probably correct according to the highest detected m/z, but the structure could not be identified with certainty as it was not included the in the used database of mass spectra, the NIST 08 Mass Spectral Library (https://chemdata.nist.gov/dokuwiki/doku.php?id=chemdata:start).

The chromatogram recorded during the analysis of bio-oil is displayed in Figure 2 and Figure 3. Data about the species identified during the analysis are given in Table A1 in appendix. Experimental mass spectra recorded during the analysis the bio-oil provided by Vertoro are displayed in appendix with potential species assignment (from Figure A1 to Figure A4).



2.2.2. Chromatogram obtained for the analysis of the Vertoro bio-oil.





Figure 3 - Second part of the chromatogram recorded during the analysis of the bio-oil.

2.2.3.GCxGC analysis of the Vertoro bio-oil

The bio-oil had to be concentrated as it was too diluted. Solvent was partly removed using vacuum distillation under ambient temperature. Injection mode was splitless to maximize the injected amount of sample and the chance to identify trace compounds. Obtained GCxGC-MS 2D maps are shown in Figure 4 to Figure 6. The concentrated sample gave us clearer signals for minor compounds however some of the lighter analytes were lost in the distillation process. Moreover, it is too concentrated for major species and large peaks tends to leave a tail, polluting or covering following peaks and preventing a good exploitation of MS spectra. No system is perfect, and an optimum must be found between maximizing the amount of trace species and having interferences due to major species peak tailing.



Figure 4 - GCxGC-MS chromatogram of the Vertoro bio-oil (part I).

The identification confirmed the data obtained with the GC-MS-FID. The bio-oil is mainly composed of oxygenated aromatics (phenolic compounds). Phenols, benzyl alcohols, phenolic ethers and benzoic acids were the most present oxygenated aromatics. Smaller carboxylic acids and esters were also found. All the above compounds were previously found in other lignin derived bio-oils as reported in previous studies (95–97). It is to be noted that *n*-dodecane was added as an internal standard by Vertoro. Additionally, multiple fatty acid methyl esters were found. The formation of such compounds as a result of lignin depolymerization and reductive hydroprocessing seems highly improbable. It was most likely the result of contamination, or due to their presence in the feedstock.



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Figure 5 - GCxGC-MS chromatogram of the Vertoro bio-oil (part II).



Figure 6 - GCxGC-MS chromatogram of the Vertoro bio-oil (part III).

Quantitative analysis of the bio-oil was done using internal standards; alkanes were chosen as internal standards for their well-defined ECN (Equivalent Carbon Number). Experimental relative response factor and ECN of anisole, toluene, *m*-cresol and *o*-guaiacol were measured. Known samples were prepared and analysed using GCxGC-FID. Calculated relative response factors and ECN are detailed in

Table 1. Results showed that the presence of an oxygenated function in the analysed aromatics influence the ECN. However, a clear group contribution of phenol and methoxy could not be found. Moreover, the contribution of a methyl group on an aromatic (e.g., toluene) was not clear either. This result deviates from group contribution to ECN found in other studies (94,98) highlighting the difficulties in quantifying this class of compounds.

										An	alytes	
			An	alytes					Anisole	Toluene	m-cresol	o-guaiacol
		Anisole	Toluene	m-cresol	o-guaiacol			Formula	C ₇ H ₈ O	C ₇ H ₈	C7H8O	C ₇ H ₈ O ₂
	Octane	0.95	0.85	0.92	1.07			Octane	7.93	7.60	8.24	8.11
S	Decane	1.31	1.12	1.28	1.51		ences	Decane	5.79	5.82	5.93	5.79
ence	Undecane	1.32	1.12	1.29	1.52			Undecane	5.77	5.79	5.90	5.74
efer	Tridecane	1.31	1.11	1.27	1.50		efere	Tridecane	5.84	5.86	5.99	5.82
æ	Tetradecane	1.38	1.17	1.35	1.59		æ	Tetradecane	5.54	5.55	5.66	5.51
	Pentadecane	1.37	1.17	1.34	1.59	(-)		Pentadecane	5.57	5.57	5.70	5.53
			•			(a)		•	•	•	•	

Table 1 – Relative response factor (a) and experimental ECN analytes (b).

Weight percentages were calculated relatively to the total detected weight excluding solvent. Since multiple internal standards were used, the average results were considered. Many of the minor analytes detected in GCxGC-MS were not detected in GCxGC-FID, either because of their very low concentration or their poor response in FID. An overview of quantified compounds is given in Figure 9.



Figure 7 - Vertoro bio-oil composition (GCxGC-FID).

These results were compared to those obtained in the previous analysis using GC-FID (Figure 8). Only analytes detected in both analyses are represented. They amount to over 98% of detected weight for GCxGC and 95% for GC. They were similar for most detected analytes. A notable difference was the detected quantity of 2,6-dimethoxy-phenol. In GC it represented 0.08% of detected weight while in GCxGC it represented between 10 and 12% of detected weight. This difference can hardly be explained by an evolution of the sample over time due to evaporation or degradation. A more probable explanation is the misattribution of peaks in GC since there was a co-elution, while the peak is clearly separated in GCxGC.







Figure 8 - GCxGC-FID and GC-FID comparison (2D FID only is GCxGC-FID but with the column directly connected to the FID and the MS is not used at all).

Overall, the two analyses led to very similar results for the Vertoro bio-oil except for one compound. For this one the GC-MS-FID data is probably more reliable. There are also still some interrogations about the identification of minor compounds. Characterization of bio-oil is a complex task and there is still progress needed to improve this type of analyses. Nevertheless, the present work highlights the formation of many phenolic compounds, especially anisole, *o*-cresol, *o*-guaiacol, and propyl-guaiacol, which is significantly heavier. These quantitative data from these analyses are suitable for making a decision in the composition of a possible surrogate.

2.3. Analysis of the sample provided by Aalto

The analysis of the bio-oil provided by Aalto was performed following the same procedure as that used for the analysis of the bio-oil provided by Vertoro. Both mass spectrometry and flame ionization detector were used for the identification and the quantification, respectively.

2.3.1. Mass composition of the Aalto bio-oil

This bio-oil is also mainly composed of phenolic compounds, but its composition is quite different from the previous one provided by Vertoro (Figure 9). This is likely because of differences in raw material, solvent and processing. This bio-oil also contains some fatty acid ethyl esters probably originating from triglycerides present in the raw material. Some ethers were also identified, probably originating from reactions of the solvent (ethanol).

EHLCATHOL – 101006744 – D6.2 - EHL-derived molecular surrogate compositions







Figure 9 - Composition of the bio-oil (solvent taken apart).

As far as phenolic compounds are concerned, significant amount of 4-ethylphenol was observed. Another species produced in significant amount is benzenepropanoic acid, 4-hydroxy-, methyl ester, a phenolic compound with a side chain composed of an ester group. Several of these species were observed in the bio-oil provided by Aalto, whereas this was not the case in the bio-oil provided by Vertoro. Table A2 in appendix gives names, global formulae, molecular weights, structures and mass fractions of the species quantified using the GC-MS-FID setup. Mass fraction (in %) were calculated without considering the huge amount of solvent (ethanol) in the mixture.

2.3.2. Chromatogram obtained for the analysis of the Aalto bio-oil.

Figure 10 to Figure 12 display the MS-chromatogram recorded during the analysis of the bio-oil as well as the structures of species identified from the comparison of recorded and literature mass spectra. Mass spectra recorded during the analysis the bio-oil provided by Aalto are displayed with potential species assignment in Figure A5 to Figure A11 in appendix.

EHLCATHOL – 101006744 – D6.2 - EHL-derived molecular surrogate compositions





Figure 10 - First part of the MS-chromatogram recorded during the analysis of the bio-oil. Anisole was added by Aalto after bio-oil synthesis.



Figure 11 - Second part of the MS-chromatogram recorded during the analysis of the bio-oil.





Figure 12 - Third part of the MS-chromatogram recorded during the analysis of the bio-oil.

2.3.3.Analysis by GCxGC.

An analysis of the bio-oil provided by Aalto was performed using two-dimensional gas chromatography. The chromatogram is displayed in Figure 13. The identification of species detected with the GC-MS-FID analysis was confirmed by the present one. As for the bio-oil provided by Vertoro, it was not possible to identify minor species. Species names are indicated in the legend of Figure 13. The mass spectra of the species are provided in appendix. No quantification attempt was made for this bio-oil using the GCxGC-FID signal as the GC-FID already gave exploitable data.



Figure 13 – GCxGC chromatogram recorded during the analysis of the bio-oil provided by Aalto. Species identification: 1) Diethyl-ether; 2) 1-Butanol; 3) 1,1-Diethoxyethane; 4) 3-Methyl-2-butanol; 5) 1-Diethoxy-butane; 6) Anisole; 7) Phenol; 8) 3-hexenoic acid, ethyl ester; 9) o-Guaiacol; 10) 1,1-Diethoxy-2-methylpropane; 11) 2-Ethylphenol; 12) 2-Ethoxyphenol; 13) 4-Ethylphenol; 14) 4-Ethylguaiacol; 15) 2,5-Diethylphenol.



2.4. Conclusion about sample analysis

Two bio-oils provided by partners of the consortium have been analyzed in detail using gas chromatography. Two-setups were used: classic gas chromatography and two-dimensional gas chromatography. Species identification was performed using mass spectrometry (by comparison with literature mass spectra when available). Quantification was performed using the FID signal relatively to the addition of an internal standards. These bio-oils are mainly composed of phenolic compounds, **cresol**, **guaiacol**, **propylguaicol**, being representative of smallest ones in the case of the Vertoro bio-oil, and **guaiacol**, **4-ethylphenol** in the case of the Aalto one. They also contain heavy esters likely coming from the trans-esterification of triglycerides present in the feedstock. They also contain many minor compounds that could not be identified, highlighting the complexity of the chemistry occurring during the depolymerization processes. These data are meaningful for the design of surrogates for practical fuels. However, it appears that these biofuels cannot be directly used in actual engines due to very different physical and kinetic properties. These difficulties may be overcome if they are incorporated to practical fuels.



3.Molecular composition of the surrogates proposed to represent EHL-derived fuels in the WP6 experimental work

Based on the bibliographic review and sample analyses presented in D6.1 and D6.2, a virtual meeting was held in July 13th between the Nancy group and Y. Li and M. Boot in order to finalize the definition of the surrogates to be used in combustion experiments. As the literature is already rich in kinetic measurements concerning the combustion of anisole, no experiment concerning this neat reactant was planned.

Concerning flame velocity measurements, which are part of task 6.3, in addition to acetone, representative of solvent, toluene, styrene, xylene isomers, phenol, benzaldehyde, anisole, o-guaiacol, cresol isomers and phenylethanol, for the neat fuel of which, measurements are currently in progress. It was decided to consider ternary gasoline surrogate made of 13.7% (vol.) *n*-heptane, 42.9% iso-octane, 43.4% aromatics, which correspond to RON 98 when toluene is used, using instead of toluene oxygenated aromatics, such as phenol, anisole, o-guaiacol, cresol isomers, ethylphenol, phenylethanol, 4-propylanisole, ethyl guaiacol and propyl anisole.

For oxidation studies in the JSR, to keep at its maximum the ability to quantify pollutants, only neat fuels will be investigated. Acetone, toluene, and xylene isomers were previously investigated. The next compounds to be studied are cresol isomers, and phenol, the chemistry of which is at the centre of that of aromatic oxygenates. As is shown in D6.1, the melting and boiling points of other possible oxygenated aromatics will not allow using them as a neat fuel in a JSR. In addition, since there is no JSR data for styrene, a compound representative of arenes with an alkenyl chain; JSR experiments with this fuel are planned.



4.Conclusion

The objective of the first task planned in WP6 was the characterization of the composition of the fuels derived from enzymatic hydrolysis lignin (EHL) and the definition of the associated molecular substitutes to be used in the two experimental tasks, 6.3, Measurement of adiabatic laminar flame velocities, and 6.4, Measurement of fuel reactivity and pollutant formation in flow reactors for surrogate molecules and for real EHL-derived fuels.

For this purpose, based on a comprehensive bibliographic data review, Deliverable 6.1 presents the chemical structures, physical properties, and global combustion performance indicators for the oxygenated aromatics and the arenes present in EHL derived fuels, as well as a review on the kinetic studies presenting ignition delay times, laminar flame velocities, and product quantifications for oxygenated aromatics. This deliverable was the basis of the paper entitled 'Possible use as biofuels of monoaromatic oxygenates produced by lignin catalytic conversion: A review' published in 2022 in Catalysis Today. This paper was the fruit of a collaboration between project partners from Aalto University and LRGP in France.

To complete this first work, Deliverable 6.2 describes the combustion kinetic studies for arenes, which were detected as potential EHL derived fuels obtained through processes including an additional hydrogenation step. It also presents the results of the chemical analysis using gas chromatography of two samples of EHL bio-oils, respectively provided by Vertoro and Aalto. Despite significant differences in their composition, both bio-oils contain an important fraction of monoaromatic oxygenates, especially phenolic compounds, such as anisole, cresol, ethyl phenol, guaiacol, and propyl guaiacol.

Based on the bibliographic review, the sample analyses presented, and scientific discussion with Vertoro and Aalto organized in July 2022, it appears that these biofuels cannot be directly used in actual engines due to very different physical and kinetic properties. These difficulties may be overcome if they are incorporated to practical fuels. Thus, surrogates consisting of neat fuels or of *n*-heptane / *iso*-octane / aromatics ternary blends with a wide range of monoaromatic hydrocarbons (toluene, xylene isomers, styrene) and oxygenates (phenol, anisole, o-guaiacol, cresol isomers, ethylphenol, phenylethanol, 4-propylanisole, ethyl guaiacol and propyl anisole) will be considered in WP6 experiments. Blends will only be used for flame velocity measurements and neat fuels will only be used when their melting and boiling points will allow it with the up-dated experimental set-ups.



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6.Appendix

6.1. Detailed information about species identified in the bio-oil from Vertoro.

Table A gives names, global formulae, molecular weights, structures and mass fractions of the species quantified using the GC-MS-FID setup. Mass fraction (in %) were calculated without considering the huge amount of solvent (methanol) in the mixture.

Table A1 - Properties of the species present in the bio-oil.

Name	Global formula	MW (g.mol⁻¹)	Structure	Mass %
2,2-dimethoxypropane	$C_5H_{12}O_2$	104.1476		25.59
anisole	C7H8O	108.1378		13.08
p-cresol	C7H8O	108.1378	OH	11.29
p-guaiacol	C ₇ H ₈ O ₂	124.1372	OH	0.16
o-guaiacol	C ₇ H ₈ O ₂	124.1372	OH	11.42
<i>n</i> -dodecane	C ₁₂ H ₂₆	170.3348		0.53





Table A – Continued.				
benzofuran	C ₈ H ₆ O	118.1326		1.89
2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	150.1745	OH	1.85
Phenol, 2,6-dimethoxy- (syringol)	$C_8H_{10}O_3$	154.1632	OH	0.08
Phenol, 2-methoxy-4-propyl-	$C_{10}H_{14}O_2$	166.2170	OH	0.59
Phenol, 2-methoxy-4-propyl-	$C_{10}H_{14}O_2$	166.2170	OH	23.97
3,5-dimethoxy-benzaldeyde (structure to be confirmed because not in the database)	$C_9H_{10}O_3$	166.1739		1.09









Table A – Continued.







6.2. Experimental mass spectra of species detected in the Vertoro bio-oil

Mass spectra recorded during the analysis the bio-oil provided by Vertoro are displayed below with potential species assignment (from Figure A to Figure A).



Figure A1 - Mass spectra recorded during the analysis of the Vertoro bio-oil (part I).





Figure A2 - Mass spectra recorded during the analysis of the Vertoro bio-oil (part II).





Figure A3 - Mass spectra recorded during the analysis of the Vertoro bio-oil (part III).





Figure A4 - Mass spectra recorded during the analysis of the Vertoro bio-oil (part IV).





6.3. Detailed information about species identified in the bio-oil from Aalto.

Table A gives names, global formulae, molecular weights, structures and mass fractions of the species quantified using the GC-MS-FID setup. Mass fraction (in %) were calculated without considering the huge amount of solvent (ethanol) in the mixture.

Table A2 - Properties of the species present in the bio-oil provided by Aalto.

Name	Global formula	MW (g.mol ⁻¹)	Structure	Mass %
1-Butanol	$C_4H_{10}O$	74.1216	HO	12.8
1,1-Diethoxyethane	$C_6H_{14}O_2$	118.1742		12.6
3-Methyl-2-butanol	$C_5H_{12}O$	88.1482	HO	4.3
1-Diethoxy-butane	C ₈ H ₁₈ O ₂	146.2273		6.2





















EHLCATHOL – 101006744 – D6.2 - EHL-derived molecular surrogate compositions



Table A – Continued.













6.4. Mass spectra of species identified in the bio-oil provided by Aalto.

Mass spectra recorded during the analysis the bio-oil provided by Aalto are displayed below with potential species assignment (Figure A to Figure A).



Figure A5 – Mass spectra recorded during the analysis of the Aalto bio-oil (part I).







Figure A6 – Mass spectra recorded during the analysis of the Aalto bio-oil (part II).



2.0

1.5

1.0

0.5

0.0

30

Signal (a.u.)

3.0

2.0

1.0

0.0

30

50

70

Signal (a.u.)





dd.

70

m/z

90

110

130

50

4

0

30



90

m/z

110

130

150







Figure A8 – Mass spectra recorded during the analysis of the Aalto bio-oil (part IV).







Figure A9 – Mass spectra recorded during the analysis of the Aalto bio-oil (part V).







Figure A10 – Mass spectra recorded during the analysis of the Aalto bio-oil (part VI).





Figure A11 – Mass spectra recorded during the analysis of the Aalto bio-oil (part VII).

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