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Evaluation of the Influence of Stainless Steel and Copper on the Aging Process of Bio-Oil

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The thermal stability of bio-oils obtained from softwood bark (SWBR) and hardwood rich in fibers (HWRF) residues was studied under aging conditions at 80 °C in sealed glass bottles in the presence of stainless steel and copper. SWBR-derived bio-oil separated into oily and aqueous phases during aging, while HWRF-derived oil remained as a single phase during the entire aging period. Dynamic rheological tests and GPC analyses were used to follow the effect of aging on the properties of bio-oils. Bio-oil aging was determined following the changes in bio-oil macrofractions using solvents of different polarities. The main difference observed between the oils analyzed was the tendency of SWBR to form materials insoluble in methanol, while HWRF aging reactions led to the formation of compounds insoluble in water and CH_2Cl_2. Methanol-insoluble and water-/CH_2Cl_2-insoluble fractions of aged oils were characterized by thermogravimetry, GPC, and Py−GC/MS techniques. The bio-oil aging reactions seem not to be affected by the presence of metals.

1. Introduction

There is universal concern about the widespread use of fossil fuels producing large amounts of carbon dioxide responsible, in part, for global warming. Fuel produced from renewable resources, such as biomass residues, are attracting growing interest, because of their environmental benign effects. Biomass-derived pyrolysis oils can find a wide range of applications in industrial heating, steam production, or in power generation.[1−3] These liquids are, however, very different from light and heavy petroleum-derived fuels.

Bio-oils may contain char particles and substantial amounts of water and have relatively high viscosity. These oils have also a very distinct, penetrating odor. Their calorific value is lower when compared to heavy fuel oil (18−25 MJ/kg vs 40 MJ/kg). Their low thermal stability is responsible for serious nozzle plugging problems and phase separation in storage tanks. This is one of the major problems limiting the use of bio-oils as commercial fuels. Low thermal stability is known to be caused by the reactivity of many compounds present in bio-oils.[1−3]

Diebold[4] conducted a phenomenological analysis of bio-oil aging mechanisms and stated that many reactions that normally were thought to require catalysis were in fact occurring without the addition of any catalyst during a long storage period. He suggested, based on theoretical backgrounds, that the main reactions responsible for bio-oil aging were (a) dehydration; (b) esterification of organic acids; (c) reaction between aldehydes, ketones, and water to form hydrates; (d) acetal formation of aldehydes and alcohols; (e) resin formation from aldehydes and phenols; (f) aldehydes and proteins that form heavy compounds; and (g) air oxidation of alcohols and aldehydes to form more acids.

Due to the large number of chemicals composing the bio-oils, following the reactivity for each individual compound during aging is not practical. This is why bio-oil aging has been commonly studied by measuring some bulk physicochemical properties, such as changes in viscosity,[4−11] changes in molar mass distribution,[4,6−10] through the determination of functional groups (using IR techniques),[7] or following changes in the content of different macrofractions.[5] During aging, there are no clear changes in pH values.[5] The changes in contents of carboxylic acids and light alcohols (determined by GC/MS) are not evident.[5] The lack of changes in bio-oil acid content during aging in closed bottles (with a limited amount of oxygen in the empty space) suggests that under these conditions bio-oil compounds are not significantly oxidized to form more carboxylic acids. Changes in IR spectra suggest[7] the reduction of C−OH groups and the formation of C−O−C bonds during aging. The increase in carbonyl groups has been associated with the oxidation of some bio-oil compounds.[7] The contribution of

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aldehydes and ketones (determined by GC/MS) to the aging process has been clearly identified.[5] It has been shown that water-soluble fractions are converted during aging into oligomeric water-insoluble compounds.[5] The mechanism leading to the formation of such heavy compounds is similar to that associated with the production of Novalak resin.[4] The separation of bio-oils derived from forest residues in two phases at aging times as short as 24 h at 80 °C has been observed.[5]

Many authors[6,7,11,12] studied the aging of bio-oil and the effect of additives (methanol and ethanol) during aging. These tests have been conducted in plastic or glass bottles. However, the aging of bio-oils in industrial applications will occur in storage tanks and in the feeding system built of stainless steal or copper. Corrosion of metals by bio-oils derived from softwood bark residues has been reported recently.[13] However, the potential catalytic effect of the metals on bio-oil aging has not been addressed in the literature. This kind of study is critical to prove whether the tests carried out in plastic or glass bottles adequately describe the aging phenomena observed under industrial conditions.

In view of the possible interaction between bio-oil and metals, the purpose of this paper is to describe the aging characteristics of bio-oils obtained from softwood bark (SWBR) and hardwood rich in fibers (HWRF) in the presence of stainless steel and copper. In this paper, only the aging characteristics of SWBR and HWRF bottom layers are studied. The effect of extractives-derived compounds on bio-oil aging is also investigated.

2. Experimental Section

2.1. Feedstock. Two biomass feedstocks were used. The first feedstock was a mixture of softwood bark originating from a pulp and paper plant debarking operation. This feedstock was made of 75.9% bark powder, 20.5% wood fibers, and 3.6% of cork on a mass basis. The feedstock, herein called "softwood bark residue" (SWBR), was composed of three softwood species: 40% white spruce (*Picea glauca*), 40% balsam fir (*Abies balsamea*), and 20% larch (*Larix laricinae*).

The second feedstock contained 34.6% bark, 65.3% fibers, and 0.1% cork on a mass basis. This feedstock originated from two hardwood species: approximately 70% aspen poplar (*Populus* spp.) and 30% white birch (*Betula papyrifera*). This material was called "hardwood rich in fibers" (HWRF). Both biomass feedstocks were pyrolyzed under vacuum at 500 °C in laboratory-scale (HWRF) and pilot-scale (SWBR) reactors. The whole liquid produced in the laboratory (HWRF) was mixed and then evaporated at 40 °C during 2 h in a rotary evaporator (Buchi, RE 111). This process was carried out in order to reduce the content of water and other volatile compounds and to obtain an oil similar to the one produced in our pilot plant, where two scrubbing towers are used. The bio-oil produced separated in two layers during storage.[14] A detailed chemical characterization of these feedstocks and their derived oils can be found elsewhere.[14] In this paper, only the bottom layers are investigated. The aging characteristics of the SWBR upper layer has been reported elsewhere.[9]

2.2. Bio-Oil Aging Tests. The study of bio-oil thermal stability during storage was carried out under accelerated aging conditions at 80 °C. In these tests, the pyrolysis oil samples were stirred in storage bottles in order to ensure their homogeneity. Approximately 45 g of oils were poured into 60 mL glass bottles. The bottles were tightly closed and preweighed before being placed in a heated oven for a specified aging time. The bottles were re-tightened each day during the storage period. After a certain aging time (defined by the experimental program), the bottles were cooled to 25 °C in a water-bath and the final mass was measured. In all cases, the mass loss increased with aging times due to the leak of some vapors. Losses smaller than 1% were obtained for aging times shorter than 100 h. Losses were in all cases smaller than 3% after 264 h of aging. The effect of metals on bio-oil aging was studied by adding metal strips into the aging bottles. The strips used were approximately 10 mm in width, 30 mm in length with a thickness of 0.6 and 1.0 mm. They were made of either copper or stainless steel (SS 316).

2.3. Molar Mass Distribution. Molar mass distribution was determined by gel permeation chromatography (GPC) using a Waters 510 pump with 410 refractive index detector. The tests were performed using *N*,*N*-dimethylformamide (DMF) as eluent at a flow rate of 1 mL/min. Bio-oil samples were dissolved in the DMF solution at a concentration of 0.2% by mass and filtered with a 2-μm filter before analysis. The injection volume was 20 μL. All the data were analyzed using Millennium 3.05 software from Waters. Calibration was based on poly(ethylene glycol) standards.

The prepared DMF solution contained 0.4 g of trichloroacetic acid (TCAA) and 0.0435 g of LiBr per liter of solution. The addition of LiBr and TCAA to the solvent disrupts molecular association by shielding the dipoles of individual molecules. Four Shodex columns in series were used in these tests: KD-803 [exclusion range (ER), 10^3 to 7×10^4 g/mol; pore diameter, 100 Å], AD 802.5/S (ER, 200 to 2×10^4 g/mol; pore diameter, 80 Å), KD-802 (ER, 100 to 5×10^3 g/mol; pore diameter, 60 Å), and AD 802/S (ER, 100 to 5×10^3 g/mol; pore diameter, 60 Å). These columns were packed with porous styrene−divinylbenzene copolymer gels.

2.4. Dynamic Rheological Studies. Dynamic rheological measurements were conducted in a controlled-strain advanced rheometrics expansion system (ARES) using parallel plates (plate diameter of 40 mm and gap 0.5 mm) at 35 °C. Strain sweep experiments at a frequency of 1 Hz were performed for freshly prepared samples that were not subjected to strain (except a small, unavoidable strain when mounting the sample on the rheometer).

2.5. Separation of Aged Oils in Fractions and Water Content Determination. Prior to performing bio-oil separation, the water content of the aged oil samples was determined by Karl Fisher titration (ASTM D-1744). Seven grams of bio-oil samples was first extracted using 200 mL of toluene. This operation was performed in order to separate some of the wood extractive-derived compounds. Waxy materials that remained in suspension in toluene were separated using a Whatman no. 42 filter. Toluene insoluble fraction was solubilized in 200 mL of MeOH and filtrated with a Whatman no. 42 filter to remove char, nonpolar waxy materials and other insoluble oligomeric compounds. The solvents were eliminated from the filtered liquids in a rotary evaporator and the dry residues were weighted. The sticky MeOH soluble fraction was solubilized again in MeOH (5 mL of MeOH per 1 g of oil). A 10-g MeOH/bio-oil mixture was added dropwise to 300 mL of ice-cooled distilled water under agitation. This step was necessary because the precipitation is quite difficult without the presence of MeOH for very viscous aged bio-oils. The water-insoluble fraction was removed by filtration with Whatman paper no. 42. The solid residues were washed with distilled water during 1 h and further extracted with dichloromethane until the filtered liquid was colorless. The solid remaining in the filter was dried at 105 °C overnight. Finally, dichloromethane was removed in a rotary evaporator at a temperature of 40 °C. The losses during solvent evaporation were reported as volatiles.

2.6. Thermogravimetric Analyses of Macrofractions. A SSC/5200 TG/DTG (220) microbalance from Seiko was used for the thermogravimetric tests. This equipment uses a horizontal differential balance mechanism. Samples of approximately 4 mg were heated from room temperature to 575 °C, under a nitrogen flow of 150 mL/min at 10 °C/min. All the tests were repeated twice to ensure good reproducibility of the results.

2.7. Py−GC/MS. Analytic pyrolysis combined with gas chromatography and mass spectroscopy (Py−GC/MS) was performed on solid samples using a CDS analytical 1000 Pyroprobe with a

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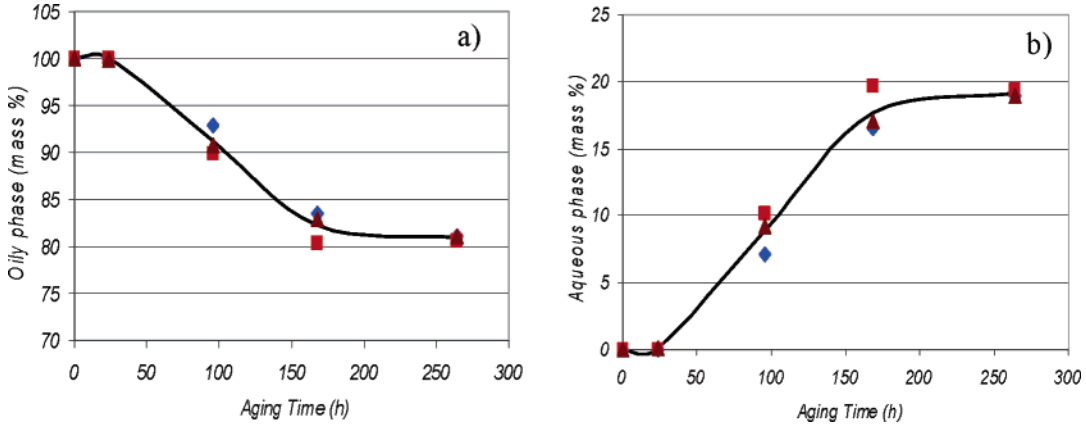

Figure 1. Separation of aqueous phase during aging at 80 °C of SWBR-derived oil (without metals and with stainless steel, copper): (a) oily phase, (b) aqueous phase.

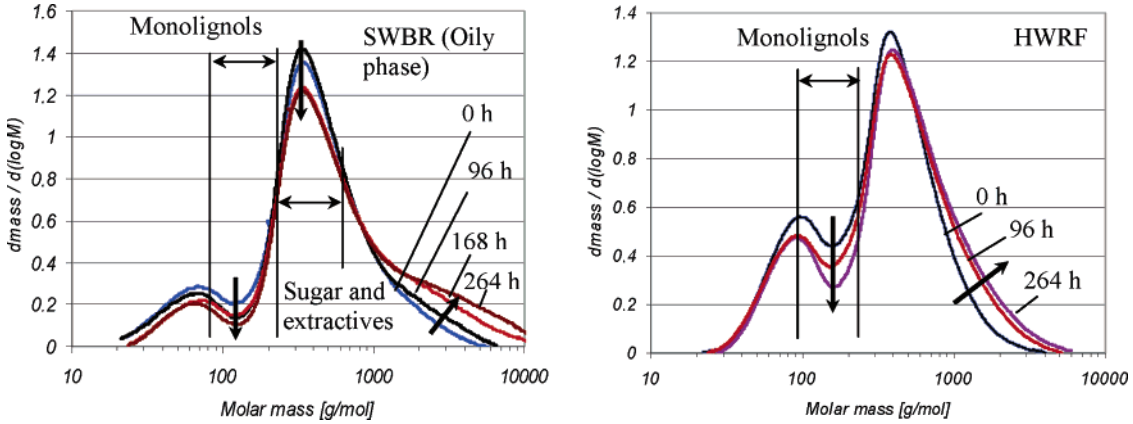

Figure 2. Changes in molar mass distribution of bio-oils during aging at 80 °C.

controlled-temperature platinum filament coupled to a HP 5890 gas chromatograph and a HP-5970 mass spectrometer. Approximately 60 mg of solid sample was placed directly inside a quartz tube. The tube was then introduced inside the platinum filament into the pyrolyzer. The filament was heated at 600 °C, and the pyrolysis products were transported to the chromatographic column using helium. Chemical species were identified comparing the mass spectra obtained experimentally with the standard compounds in a library.

3. Results and Discussion

3.1. Phase Separation during Aging. The main macroscopic difference observed between the oils investigated is the tendency of SWBR to form a separate "aqueous phase" after 96 h of aging. As shown in Figure 1, the amount of aqueous phase formed was around 20 mass % after 168 h of aging. Aqueous phase separation was also reported by Oasmaa and Kuoppala[5] after aging fast pyrolysis oil at 80 °C during 24 h.[5] On the other hand, HWRF-derived oil remained as a homogeneous oily phase. The presence of metals has no significant effect on aqueous phase separation.

The low capacity of the SWBR bottom layer to accept water and other polar compounds is a clear indication of the higher hydrophobic character of organics forming this kind of oil. This result is in agreement with the higher carbon content of SWBR bottom layer organics (61.3 mass %) compared with the HWRF organics (56.8 mass %).[14]

3.2. Changes in Molar Mass Distribution during Aging. Changes in molar mass distribution of SWBR oily phase and HWRF bio-oils during aging without metals are reported in Figure 2. The main feature observed is a clear reduction in the amount of low molar mass compounds and the formation of compounds heavier than 1000 g/mol. This phenomenon is more pronounced for the SWBR bottom layer (oily phase) due to the combined effect of the aging reaction and the removal of light compounds in the aqueous phase expelled from the bio-oil matrix. Changes in M_n, M_w, M_z,and M_{z+1} during aging are shown in Figure 3. All parameters describing the molar mass distribution increase linearly for both oils. However, the SWBR oily phase varies in mass at a much higher rate. This result is a clear indication that fuel-quality degradation, in terms of molar mass and viscosity variation during aging, is far more pronounced for SWBR-derived oil than for HWRF-derived oil.

3.3. Strain Sweep Experiments during Aging. Strain sweep tests at 35 °C for SWBR (oily phase) and HWRF at different aging times are presented in Figure 4. The bio-oil multiphase character was reported in a previous study.[15] At very low strains, storage modulus (G') is larger than loss modulus (G'') for the SWBR bottom layer "fresh" oil, indicating that the sample is an elastic physical gel made of oligomeric compounds (micelles) interconnected through weak physical bonds such as hydrogen bonds. As aging reactions progress, G' values increase, indicating that the network structure in the SWBR bottom layer becomes denser. As the bio-oil aging progresses, small covalently linked clusters form. These clusters can deform but are not normally disrupted by shear. The presence of these clusters is indicated by a second linear viscoelastic plateau (constant G'), which appears at relatively large strains. The fact that G' is lower than G'' (at relatively high strain, when the

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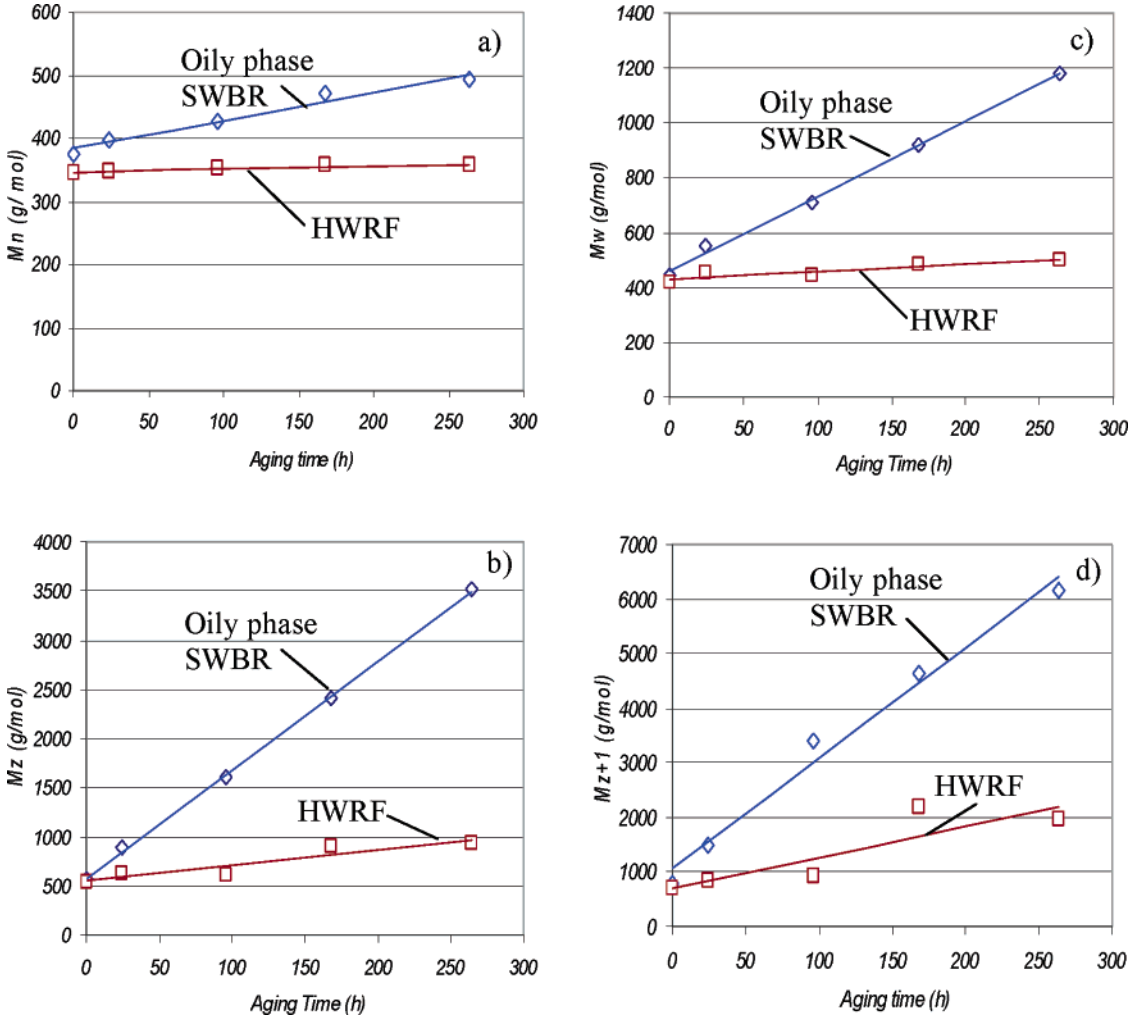

Figure 3. Changes in molar mass distribution parameters of bio-oils during aging at 80 °C: (a) M_n, (b) M_w, (c) M_z, d) M_{z+1}.

physical gel is broken) suggests that these covalent clusters do not form a continuous network covering all the bio-oil volume. Aged SWBR oily phase response includes both the physical links between some oligomeric materials and the covalent bonds in growing clusters formed during aging. Nevertheless, since the weak physical bonds are the first to break, the samples continue to show a strain at which the physical bonds are broken. The forces responsible for the formation of an interconnected network can also contribute to progressively expel or remove the aqueous phase out of the continuous network phase, like water from a sponge. This indicates also that the formation of new molecules with hydrophobic character occurs.

It is interesting to note that for HWRF fresh oils, G' is smaller than G'' at very low strains, indicating that this "fresh" oil behaves like a sol. After 96 h of aging, G' and G'' have similar values. This indicates that aging reactions have generated materials that contribute to the formation of micelles to a level high enough to form a continuous network structure covering all the bio-oil volume. These structures are believed to be formed out of micelles of heavy compounds poorly soluble in the bio-oil matrix.

3.4. Changes in Chemical Composition during Aging. Aged bio-oils were separated into five macrofractions following their successive extraction with different solvents. The content of these fractions in SWBR oily and aqueous phases at different aging times is shown in Table 1.

The concentration of water in the SWBR aqueous phase is more than 3 times that of the SWBR oily phase for the most aged samples. Water concentration of the aqueous phase increases from 34.3 to 42.6 mass % as aging progresses. Water, water-soluble, and toluene-soluble fractions are the main ones forming the aqueous phase. The methanol- and water-insoluble fractions are minor. These compounds make their way to the aqueous phase in the form of small droplets or tiny suspended particles. They are separated together with the aqueous phase by decantation.

As expected, the oily phase contains a lower amount of water and water-soluble fraction but form higher amounts of water-insoluble fractions. The content of toluene solubles is also lower.

Using the content of different subfractions in SWBR oily and aqueous phases enables one to estimate the amount of these fractions in the SWBR bottom layer. Figure 5 presents the content of water-insoluble fractions (the sum of toluene-soluble, methanol-insoluble, water-insoluble/CH_2Cl_2-soluble, and water-/CH_2Cl_2-soluble fractions) for fresh and aged SWBR and HWRF oils. The content in water-insoluble fraction increases upon aging for both oils. For HWRF samples, a plateau is reached after 100 h, while for SWBR samples the content in water-insoluble fractions tends to increase.

Figure 6 presents the evolution of each macrofraction of SWBR- and HWRF-derived oils during aging. The toluene-soluble content of the fresh HWRF and SWBR is 7.8 and 1.3 mass %, respectively (Figure 6a). It has been found that the toluene-soluble fraction of fresh HWRF and SWBR bottom layers is formed of monolignols, extractives-derived compounds, and relatively low molar mass heavy compounds.[14] The amount

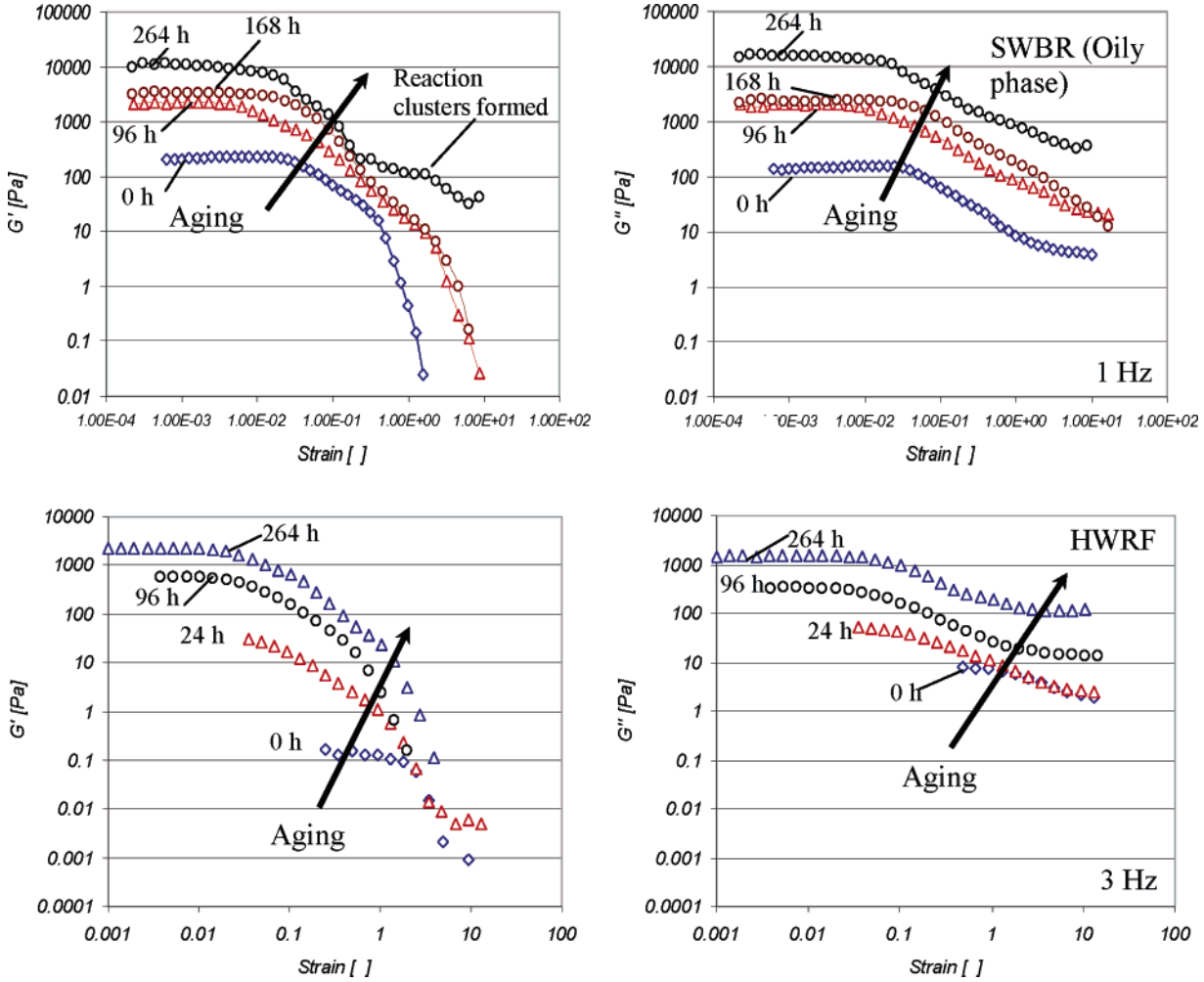

Figure 4. Strain sweep tests of SWBR (oily phase) and HWRF Oils (35 °C) at different aging times.

Table 1. Average Composition of SWBR Oily and Aqueous Phases at Different Aging Times (mass %)

fraction	0 h	24 h	96 h	168 h	264 h
Aqueous Phase (% mass)					
water	–	–	34.3	38.7	42.6
toluene-soluble	–	–	8.0	7.2	4.7
MeOH-insoluble	–	–	4.0	2.0	1.7
water-soluble	–	–	35.5	41.6	41.0
water insoluble/CH_2Cl_2-soluble	–	–	1.4	0.5	0.3
water-/CH_2Cl_2-insoluble	–	–	1.7	2.2	1.6
volatiles	–	–	15.3	7.8	8.1
total	–	–	100	100	100
mass % of aqueous phase on SWBR bottom layer basis	0	0	8.8	17.7	19.1
Oily Phase (% mass)					
water	14.6	14.1	14.2	13.9	12.5
toluene-soluble	1.3	4.3	1.7	1.0	0.6
MeOH-insoluble	2.1	1.9	8.6	13.9	23.3
water-soluble	41.3	35.7	29.7	27.3	21.2
water-insoluble/CH_2Cl_2-soluble	12.5	12.7	16.7	18.9	15.0
water-/CH_2Cl_2-insoluble	13.0	14.4	16.1	17.9	16.0
volatiles	14.2	16.9	13	7.1	11.4
total	100	100	100	100	100
mass % of oily phase on SWBR bottom layer basis	100	100	91.2	82.3	80.9

of toluene-soluble fraction first increases during the first 24 h of aging but is dimmed as the aging reaction progresses. The presence of a peak at around 24 h of aging could be explained by the formation of relatively low molar mass heavy compounds that further react to form more heavy compounds with reduced solubility in toluene.

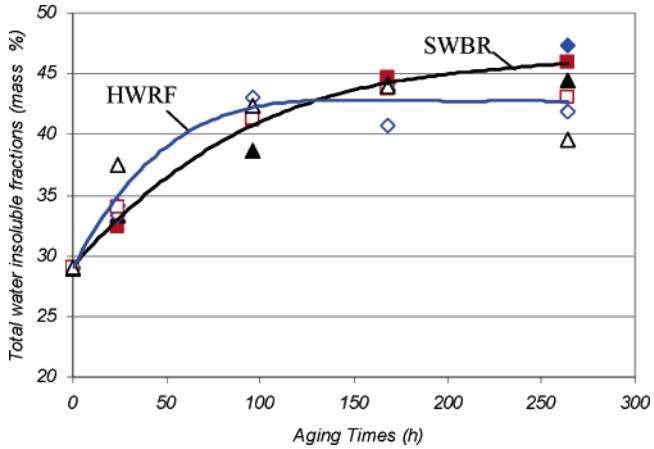

Figure 5. Changes in the composition of total water-insoluble fractions during aging (without metals and with stainless steel, copper): full, SWBR; empty, HWRF.

The water-soluble fractions are formed of benzenediols, furans, sugars, and polar heavy compounds. This fraction is consumed progressively during aging (Figure 6b), in agreement with the data reported by Oasmaa et al.[5] Benzenediols present in this fraction can participate to form phenol/formaldehyde polymers. Furans can undergo condensation reactions with the evolution of water, forming an acetone-soluble resin.[4] The mono and oligosugars also participate in the bio-oil aging process through forming heavy compounds with reduced solubility in water.

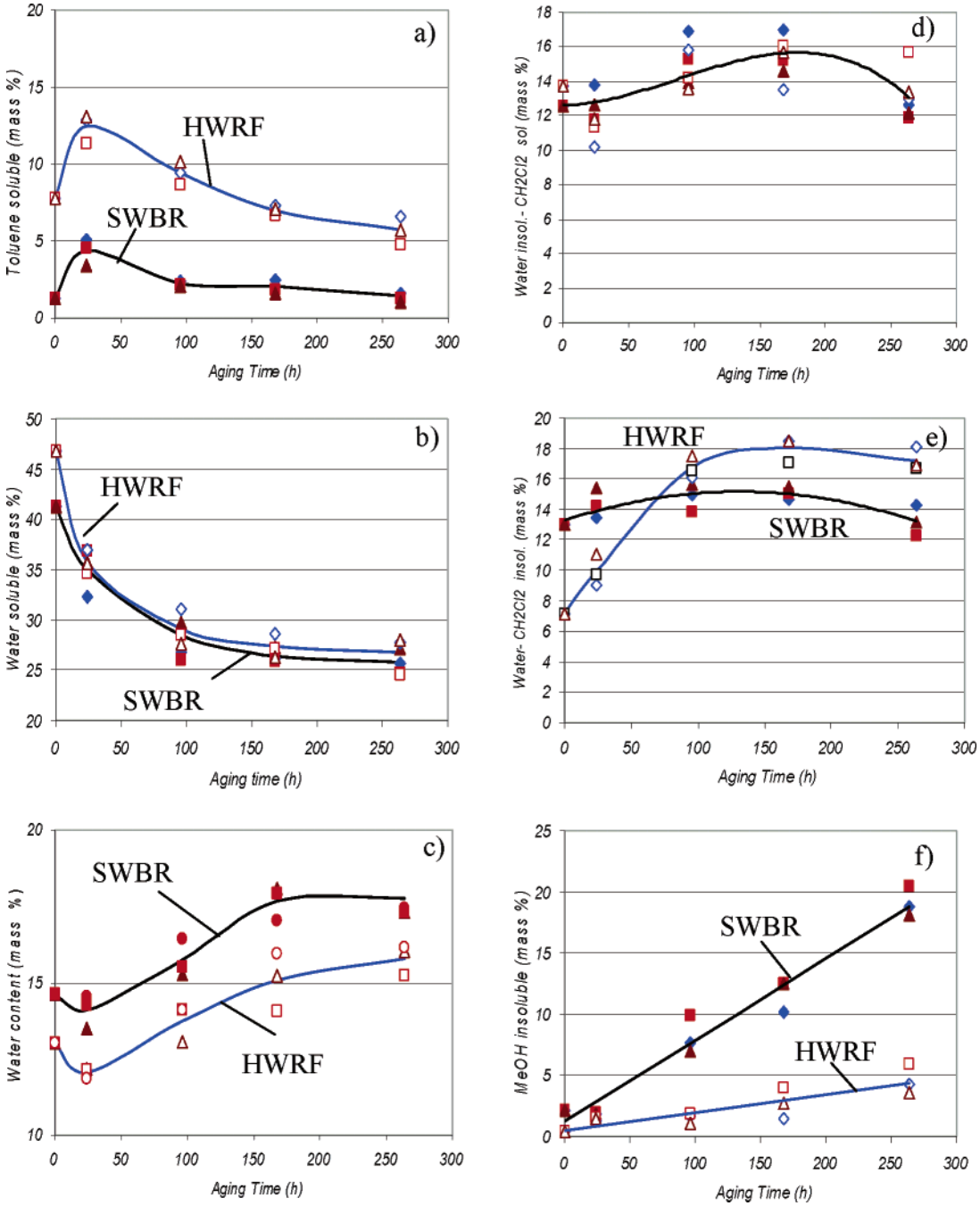

Figure 6. Changes in composition of bio-oils during aging at 80 °C (without metals, and with stainless steel, copper): empty, HWRF; full, SWBR. (a) Toluene-soluble fraction, (b) water-soluble fraction, (c) water content, (d) water-insoluble/CH_2Cl_2-soluble fractions, (e) water-/CH_2Cl_2-insoluble fraction, (f) MeOH-insoluble fraction.

The water content of fresh SWBR (14.6 mass %) is higher than that of fresh HWRF (13.0 mass %).[14] Changes in water content with aging follow a similar trend in both oils, indicating similar reaction rates for reactions associated with the formation or consumption of water (Figure 6c). The initial reduction of water content suggests that the reactions consuming water (e.g. homopolymerization, hydration) are more important in the initial aging stages than the reactions generating water (esterification, acetalization, polycondensation, alcohol addition). The water formation reactions are predominant at later aging stages.

The trends observed for the water-insoluble/CH_2Cl_2-soluble fractions (Figure 6d) are very similar for both oils. Fresh oils contain monolignols, extractives-derived compounds, and relatively low molar mass heavy compounds (538−891 g/mol).[14] The amount of water-insoluble/CH_2Cl_2-soluble fraction slightly changes over time. Oasmaa et al.[5] also reported similar results regarding the changes in the amount of this fraction (between 7.5 and 18 mass %) during aging.

The water-/CH_2Cl_2-insoluble fraction (Figure 6e) is composed of relatively heavy compounds with molar masses ranging from 1475 to 1967 g/mol.[14] It is important to observe that HWRF-derived oils have a tendency to form heavy compounds during aging. In contrast, the rate of formation of methanol-insoluble materials is 4.7 times higher for the SWBR (0.066 mass %/h) than for HWRF (0.014 mass %/h) (Figure 6f). This fraction is formed of very heavy compounds with relatively low polarity and char particles. Because of its low solubility in methanol, this fraction is expected to be insoluble in the bio-oil matrix. The presence of metals in contact with the bio-oils does not

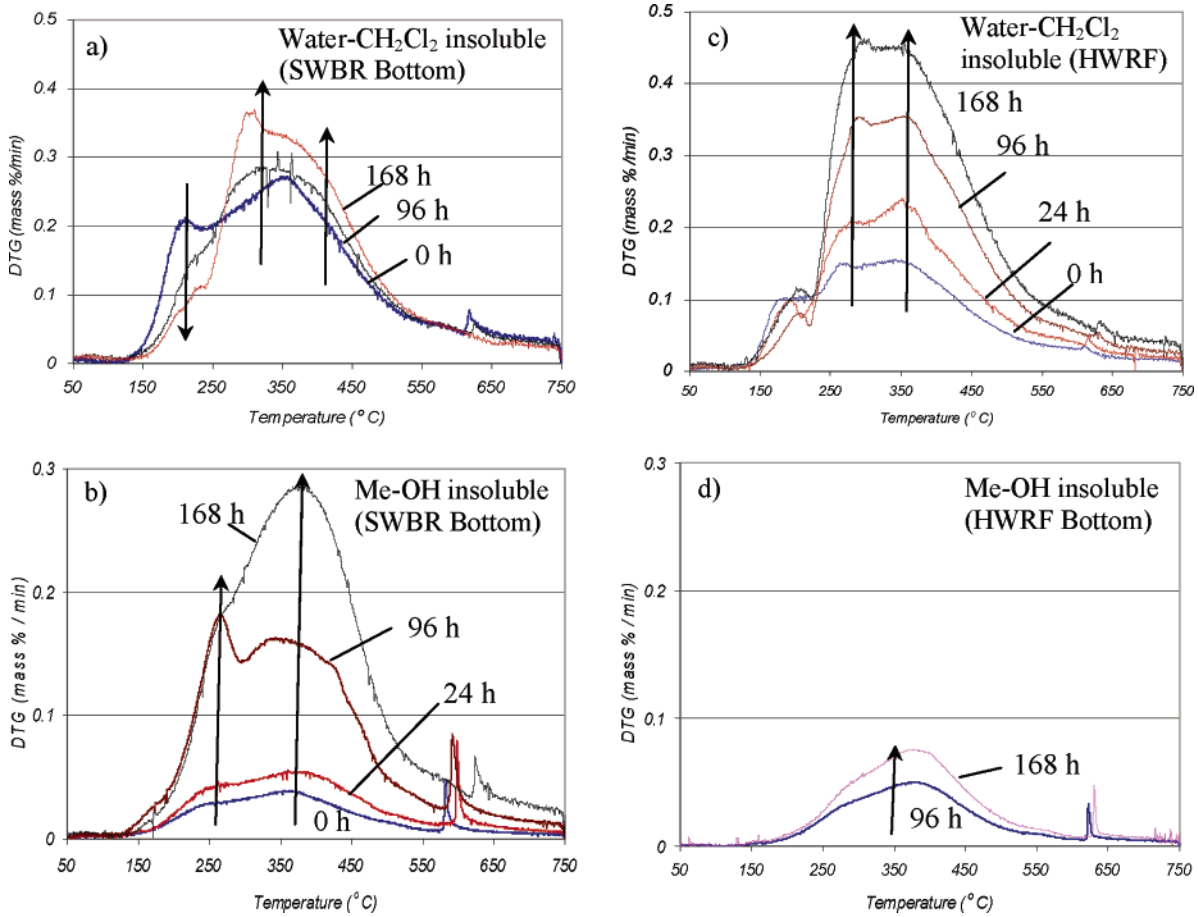

Figure 7. DTG curves of water-/CH_2Cl_2-insoluble and methanol-insoluble fractions for aged SWBR and HWRF oils. The DTG curves were multiplied by the content of each of these fractions.

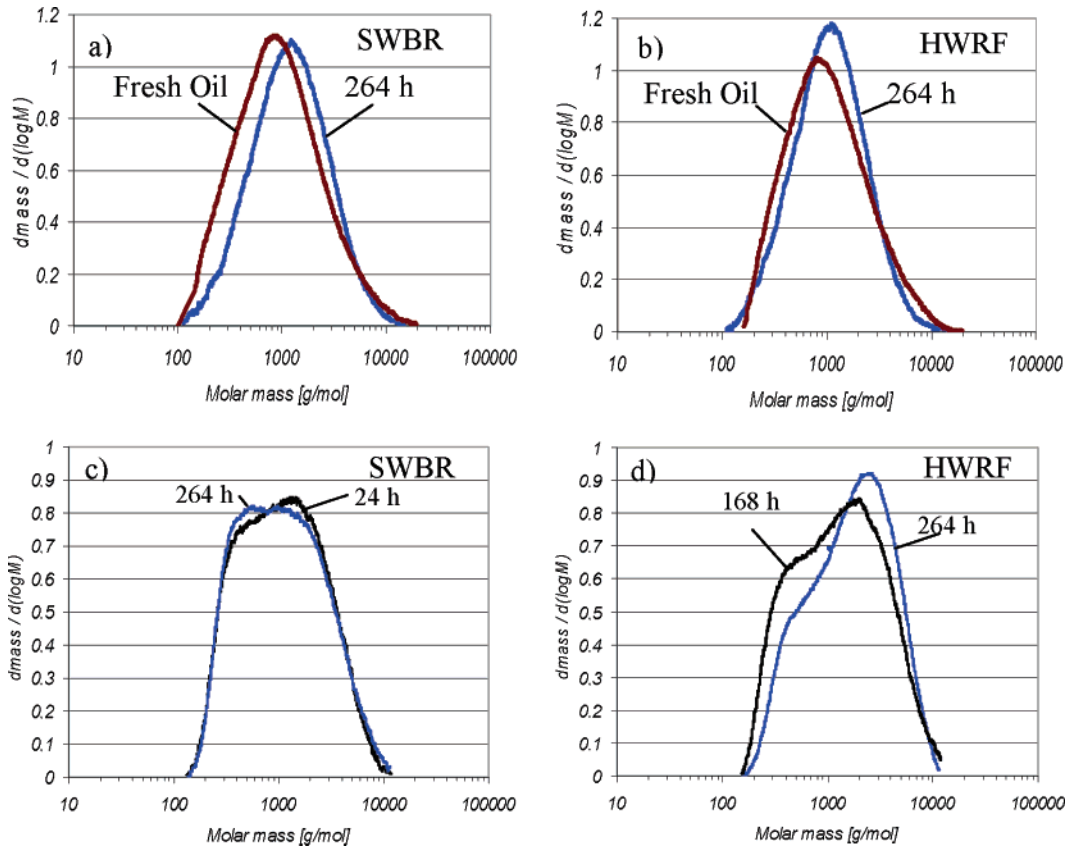

Figure 8. Changes in molar mass distribution of bio-oil fractions during aging: water-/CH_2Cl_2-insoluble fractions (a and b) and methanol-insoluble and -soluble fractions (c and d).

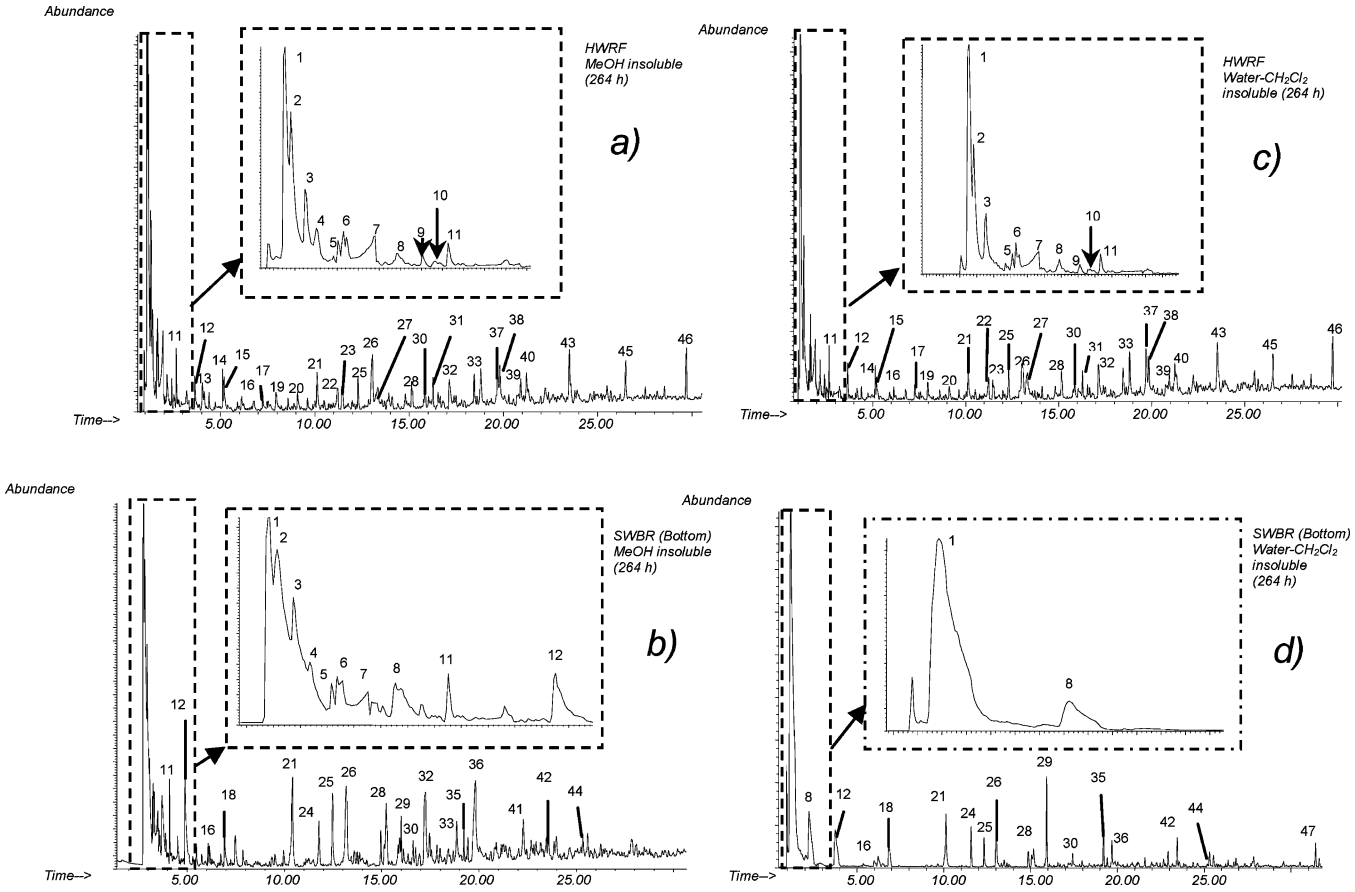

Figure 9. Py−GC/MS of water-/CH_2Cl_2-insoluble and MeOH-insoluble fraction obtained from SWBR and HWRF after aging.

seem to change the amount of each subfraction formed, the differences being smaller than the experimental noise.

It is now interesting to understand why the SWBR bottom layer has a tendency to produce methanol-insoluble heavy compounds while the aging of HWRF leads to the formation of water-/CH_2Cl_2-insoluble heavy compounds.

3.5. Thermogravimetric Analysis of Methanol-Insoluble and Water-/CH_2Cl_2-Insoluble Fractions. Figure 7 presents the differential thermogravimetry (DTG) curves for methanol-insoluble and water-/CH_2Cl_2-insoluble fractions of SWBR and HWRF oils during aging. Each DTG curve was multiplied by its respective mass fraction in oils. As such, the curves indicate the mass losses on a bio-oil basis, thus representing the progress of aging reactions.

During aging, there is a net reduction in the amount of compounds that are removed at temperatures lower than 250 °C for the water-/CH_2Cl_2-insoluble fraction of SWBR. These compounds were assigned to the weakly associated polar volatile chains.[14] New and more stable bonds may be formed during aging linking these chains to other molecules. This kind of weakly associated chain appears in the methanol-insoluble fraction (after 96 h of aging). Somehow it seems that the nature of the weakly associated chains remained without major changes during the process. It is interesting to note that the weakly associated chains are less present in HWRF and do not seem to go through major changes during aging.

Compounds decomposing between 200 and 350 °C have been assigned to some monolignol chains weakly associated with the heavy compounds. These chains increase during aging for all fractions investigated, suggesting the incorporation of monolignols to heavy compounds structure upon aging. There is also an increase of more structured heavy compounds, which crack at temperatures higher than 350 °C due to the formation of stronger chemical bonds.

3.6. Molar Mass Distribution of Water-/CH_2Cl_2-Insoluble and Methanol-Insoluble Fraction. Figure 8 presents the molar mass distribution (MWD) of water-/CH_2Cl_2-insoluble and methanol-insoluble fractions for SWBR and HWRF aged oils. The mass-average molar mass (M_w) is larger for the methanol-insoluble fractions (1571−2160 g/mol) than for the water-/CH_2Cl_2-insoluble fractions (1439−1658 g/mol).

The shape of the MWD curves is also quite different between these two fractions. The dispersion of MWD curves can be quantified by the polydispersity index (PI = M_w/M_n). The MWD of water-/CH_2Cl_2-insoluble fractions are less dispersed ($1.87 \leq PI \leq 2.12$) than for methanol-insoluble fractions ($2.18 \leq PI \leq 2.35$). The MWD for methanol-insoluble fractions for both aged oils present two clearly defined regions. The first region is centered around 550 g/mol. The second region presents a peak between 1450 and 1900 g/mol. It is interesting to note that such small heavy compounds (550 g/mol) are not soluble in methanol. It is probable that the presence of these "apparently" low molar mass compounds in the first region is due to the adsorption of heavy nonpolar compounds in the GPC columns because of the use of DMF as solvent.[14] If this hypothesis is true, then the first region may indicate the presence of "very heavy nonpolar compounds". The actual values of M_w for the methanol-insoluble fraction must be even larger than the one reported here. SWBR methanol-insolubles may include larger amounts of "very heavy nonpolar compounds".

3.7. Py−GC/MS of Water-/CH_2Cl_2-Insoluble and Methanol-Insoluble Fractions. Figure 9 presents the Py−GC/MS chromatograms corresponding to water-/CH_2Cl_2-insoluble and to methanol-insoluble fractions for both SWBR and HWRF oils.

Table 2. Py-GC/MS Chromatograms of Water-CH_2Cl_2 Insoluble and MeOH Insoluble Fractions from Aged SWBR and HWRF Oils

NO	NAME	M_W	HWRF WATER-CH_2CL_2 INSOL.	HWRF MEOH INSOL.	SWBR WATER CH_2CL_2 INSOL.	SWBR MEOH INSOL.
1	carbon dioxide	44	X	X	X	X
2	acetaldehyde	44	X	X	X	X
3	acetone	58	X	X		X
4	1,3-cyclopentadiene	66		X		X
5	2-methyl-1-butane	70	X	X		
6	2-butanone	72	X	X		X
7	acetic acid	60	X	X		X
8	benzene	78	X	X	X	
9	2-pentanone	86	X	X		
10	3-pentanone	86	X	X		
11	2,5-dimethylfuran	96	X	X		X
12	toluene	92	X	X	X	X
13	N,N-dimethylformamide	73		X		
14	2-butenedioic acid	116	X	X		
15	2-cyclopentent-1-one	82	X	X		
16	P - xylene	106	X	X	X	X
17	2-cyclopentent-1-one- 2-methyl	96	X	X		
18	styrene	104			X	X
19	2-hydroxycyclopent-2-en-1-one	98	X	X		
20	2-cyclopenten-1-one, 3-methyl	112	X	X		
21	phenol	94	X	X	X	X
22	1,2-cyclopententanedione, 3-methyl	112	X	X		
23	cyclopent-2-en-1-one-2,3-dimethyl	110	X	X		
24	indene	116			X	X
25	2-methylphenol	108	X	X	X	X
26	3-methylphenol	108	X	X	X	X
27	2-butanamine	73	X	X		
28	2, 4-dimethylphenol	122	X	X	X	X
29	naphthalene	128			X	X
30	3,5-dimethylphenol	122	X	X		X
31	2-methoxy-4-methylphenol	138	X	X		
32	1,2-benzenediol	110	X	X		X
33	3-methoxy-1,2-benzenediol	140	X	X		
34	3-methyl-1,2-benzenediol	124	X	X		X
35	2-methylnaphtalene	142			X	X
36	naphtalene-1-methyl	142			X	X
37	4-methyl-1,2-benzenediol	124	X	X		
38	1-(3-methoxy phenyl)-ethanone	150	X	X		
39	2,6 –dimethoxyphenol	154	X	X		
40	3,4-dimethoxyphenol	154	X	X		
41	4-ethyl-1,3-benzenediol	124				X
42	Acenaphthylene	152			X	X
43	2-methoxy-5-(1-propenyl)- phenol	164	X	X		
44	1-naphthelenol	144			X	X
45	1,1-diphenyl ethylene,	180	X	X		
46	2,6-dimethoxy 4-(2-propenyl)- phenol	194	X	X		
47	phenanthrene	178			X	

The compounds identified are listed in Table 2. These tests were only performed for the heavier fractions (water-/CH_2Cl_2-insoluble fractions and MeOH-insoluble fractions) because these fractions contain most of the products of aging reactions. Py−GC/MS analysis of these fractions can be very useful to identify the compounds participating in the pyrolysis process.

The chemical compositions of both fractions are similar for the same oil. This result suggests that the solubility differences observed are mainly determined by their differences in molar mass. There are, however, important differences between the HWRF- and SWBR-derived fractions. The first difference is observed in the presence of polyaromatic compounds (e.g., naphthalenes) forming the heavy fractions from SWBR-derived oils but not in the HWRF-derived fractions. The second difference is due to the absence of cyclopentents in SWBR oligomeric fractions. These compounds are quite abundant in HWRF heavy compounds. The third major difference found is the absence of dimethoxyphenols in SWBR heavy fractions. It is interesting to note the presence of acetaldehyde, acetone, and acetic acid. This can be due to the fact that some of these compounds participate in the aging reactions contributing to the formation of heavy compounds. The bonds formed, however, can be broken during the Py−GC/MS tests. The CO_2 observed might be produced from the sugars participating in the aging reactions.

The higher tendency of SWBR-derived oils to form methanol-insoluble fractions can be explained by the combined effect of these three factors. The macroscopic characteristics of both bottom layers are quite similar. Perhaps the main difference can be found in the larger amounts of benzanediols + cyclopentents + furans found in the HWRF.[14] These compounds act as good solvents, reducing the tendency of the aqueous phase to separate.

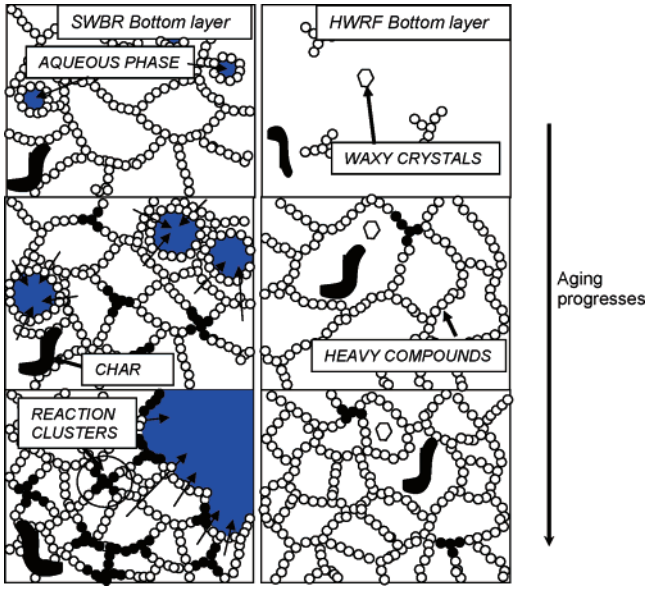

Figure 10. Changes in multiphase characteristics of bio-oils during aging.

The initial carbon content of SWBR organic compounds (61.3 mass %) is considerably larger than that of the HWRF organics (56.8 mass %).[14] These differences in polarity seem to be enough to reduce the capacity of the SWBR bio-oils matrix to accept water and other polar compounds, leading to their removal in the expelled aqueous phase. As a consequence, the newly formed heavy compounds will have a further reduced polarity (reduced hydrophilic character). The capacity of a bio-oil matrix to accept water must be considered as a key factor for bio-oil thermal stability.

The polyaromatic compounds present in the SWBR bottom layer (e.g., naphthalenes) may react with other compounds in the bio-oil matrix, forming heavy compounds with a relatively low polarity. The polyaromatic compounds in bio-oils are substituted with many functional groups. These functional groups are responsible for the participation of polyaromatic compounds in aging reactions.

The presence of dimethoxy phenols in HWRF may also play an important role in the formation of heavy compounds of relatively low molar mass. Scholze et al.[16] reported that the molar mass of water-insoluble fractions of softwood-derived oils is usually larger than that of hardwood-derived oils. This phenomenon was explained by a free C5 position for softwood lignins, which is prone to polymerization reactions.[16] The presence of dimethoxyphenols can be a factor leading to a reduction in molar mass of heavy compounds. The presence of metals during aging does not affect much of the aging process under the storage condition investigated.

Formation of heavy compounds and the reduction of light organics can likely increase the density of bio-oil network structures. In Figure 10, a scheme outlining bio-oil changes during aging is proposed. Knowing that aging reactions lead to the formation of heavy compounds, these compounds present a reduced solubility in the matrix. As such, they are expected to form miscelles that eventually can interlock to generate a network structure covering the whole bio-oil volume. This network structure is initially maintained by physical bonds but gets stronger as the formation of covalent bonds progresses. The consumption of light organic compounds and the formation of water during aging lead to the separation of phases depending on the capacity of bio-oil matrix to retain these polar compounds. Some organic polar compounds are removed together with some water as an aqueous phase during aging. As such, the heavy compounds formed in the remaining oily phase will have a reduced polarity.

4. Conclusions

The amount of water-soluble compounds decreases during aging. The compounds resulting from aging reactions are mainly heavy compounds that contribute to the formation of network structures. As the bio-oil aging progresses, small covalently linked clusters form. The presence of metal strips in contact with the bio-oil did not affect much of the bio-oil aging process under the range of time (0−264 h) and temperature (80 °C) investigated. There are important differences between the aging features of bio-oils obtained from SWBR and the ones obtained from HWRF. Fuel-quality degradation (in terms of molar mass and viscosity) during aging is far more pronounced for SWBR-derived oil than for HWRF-derived oil. The main macroscopic difference observed between the oils investigated is the tendency of SWBR to form a separate "aqueous phase" and methanol-insoluble heavy compounds. The capacity of a bio-oil matrix to tolerate water determines the resistance of these oils to form separate phases. The separation of an aqueous phase is an event that further triggers the degradation of bio-oils, leading to the formation of methanol-insoluble heavy compounds. The presence of polyaromatic compounds and the absence of dimethoxy phenols are ideal conditions for the formation of these heavy compounds.

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