

# Upgrading Technique of Sugarcane Bagasse Bio-Oil Heavy Fraction for Stability Improvement

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Energetic efficiency of sugarcane mills in Brazil has been increasing in the past decades, generating a surplus of bagasse. Even though bagasse has a low energy density, it has been used as fuel in boilers. Pyrolysis, a thermochemical process, produces bio-oil and biochar, being an alternative to increasing the energy density of biomass. In this context, bio-oil, when compared to bagasse, is more versatile in terms of use, storage, and transport. However, this biofuel is typically a viscous, acid, and thermally unstable liquid, which is harmful to engines and boilers. Furthermore, polymerization of bio-oil occurs during aging, which increases viscosity, average molar mass, and water content. In order to avoid these problems, upgrading techniques can be used. These techniques are usually applied to the whole oil. Nonetheless, the upgrading may be more effective if the bio-oil is fractionated and each fraction is processed separately. This study assessed the upgrade of the heavy fraction of bio-oil (HBO) through solvent addition. Initially, two different concentrations (10 wt. % and 15 wt. %) of methanol, ethanol, and acetone were added into HBO. The mixtures were submitted to an accelerating aging process: storage for 24 h at 80 °C. Physical properties including viscosity, pH, and water content were measured before and after storage. According to the properties analyzed, all blends met the appropriate specifications of ASTM D7544 (2017) for fast pyrolysis bio-oil. The results also indicated that all solvents had a significant effect on HBO properties, whereas their addition reduced its viscosity, improving stability. The blended HBO with 15 wt. % methanol achieved the lowest viscosity and aging rate. Therefore, in this case, methanol was more efficient than ethanol or acetone.

## 1. Introduction

Sugarcane bagasse is a fibrous material from milling and juice extraction. It is predominantly composed of 20 wt. % lignin, 25 wt. % hemicellulose, and 42 wt. % cellulose (Kim; Day, 2011). This residual biomass is very popular in Brazil due to its current agribusiness scenario, being the largest sugarcane producer since 1980 (FAOSTAT, 2019). In this way, the bagasse supply can be considered as stable and constant, which is advantageous for raising interest in this biomass conversion into biofuels and added-value products (Loh et al., 2013).

Conventionally, the bagasse is used as solid fuel through direct combustion in industrial boilers to energy cogeneration (Evans et al., 2010), but it may not be a better way of utilization because of its low energy density. Then, this biomass transformation into high-density fuels through pyrolysis is a suitable alternative (Dhyani; Bhaskar, 2017). Fast pyrolysis results in liquid and solid renewable fuels: bio-oil and biochar, respectively (Chong et al. 2017). Bio-oil can substitute fossil fuels such as heavy oil in stationary applications, but it depends on its quality and properties. This biofuel has a high viscosity, water content, acidity, and instability, which may cause combustion problems and equipment corrosiveness; so, these characteristics need to be considered on system design (Oasmaa et al., 2015).

In order to avoid issues related to bio-oil high water content, it can be fractionated in two phases: an aqueous hydrophilic light fraction (carbohydrate-derived) and a non-aqueous hydrophobic heavy fraction (lignin-derived) (Guo et al., 2010). The heavy fraction is more feasible replacing oil fuel in boilers and furnaces than light fraction due to its lower water content and higher pH and heating value. Nevertheless, this fraction

viscosity is much higher compared to the whole bio-oil (Lindfors et al., 2014), and it does not comply with the specifications of ASTM D7544 (2017) for fast pyrolysis oil. Therefore, the application of physical upgrading techniques such as solvent addition is necessary to decrease viscosity and improve stability.

The addition of a polar solvent affects bio-oil viscosity by three mechanisms: physical dilution, reactivity reduction (by molecular dilution or changes in microstructure), and chemical reactions between bio-oil components and the solvent, which prevent increased carbon chains (Xiu; Shahbazi, 2012). Mei et al. (2019), Pidtsang et al. (2016), and Fei et al. (2014) proved that methanol addition can significantly delay the aging rate of storage bio-oil as a result of its effects on polymerization and aging reactions. Despite being a green resource and providing these same effects, the results of ethanol are considered less efficient when compared to methanol. Both alcohols showed positive changes in other properties of bio-oil by increasing pH and decreasing the initial water content (Pidtsang et al., 2013; Oasmaa et al., 2004). Liu et al. (2014) and Udomsap et al. (2012) reported that the addition of acetone acts mostly by physical dilution because of its favorable performance on the properties of fresh bio-oil.

Therefore, this study aims at investigating the influence of adding different mass concentrations of three solvents (methanol, ethanol, and acetone) by evaluating and comparing their effects on sugarcane bagasse bio-oil heavy fraction physicochemical properties and stability during an accelerated aging process.

## 2. Methodology

### 2.1 Bio-oil heavy fraction

The bio-oil heavy fraction (HBO) used in this work was acquired from Bioware®: a Brazilian technology company, which produces commercial size pyrolysis plants. This fraction was produced during an industrial plant test by a fast pyrolysis process in a fluidized bed reactor at 500 °C. The light fraction was separated during the gas condensation process.

### 2.2 Experimental procedure

Three different solvents, methanol (99.8 %, Synth), ethanol (99.5 %, Sigma-Aldrich), and acetone (99.5 %, Êxodo) were added into the bio-oil heavy fraction at two different mass concentrations. The mixtures were stirred at 1,250 rpm for 3 minutes using a mechanical agitator (IKA, model RW-20). It results in six samples: 10–M, 15–M, 10–E, 15–E, 10–A, 15–A, with 10 and 15 wt. % of methanol, ethanol, and acetone, respectively. Physicochemical characteristics were measured before storage. Then, the mixtures went through a thermal treatment at 80 °C for 24 h, which accelerates the aging procedure being equivalent to the storage of one year at room temperature (Hilten; Das, 2010). The aged blends were analyzed to evaluate stability by the following physical properties: viscosity, water content, pH, and density. Each sample measurement was repeated in triplicate.

### 2.3 Samples characterization

#### 2.3.1 Viscosity

The kinematic viscosity of the HBO was measured by ASTM 7042 (2016) at 40 °C using a Stabinger Viscosimeter SVM 3000 (Anton Paar). For the mixtures, the viscosity was tested on a Cannon-Fenske (size 200) capillary viscosimeter according to ASTM 445 (2017) at 40 °C.

#### 2.3.2 Water content

The water content of the HBO and the mixtures were analyzed according to the volumetric Karl Fischer titration method (ASTM E203, 2016) using chloroform:methanol (ratio 3:1) as the solvent (Oasmaa, 2001) and HYDRANAL®-Composite 5K (Honeywell Fluka) as the titrant.

#### 2.3.3 pH

The pH value of the samples was determined using Accumet Basic AB 15 pH meter at 25 °C. Before the analysis, the instrument was calibrated with pH 4 and 7 buffer solutions.

#### 2.3.4 Density

The density of the samples was measured with the digital DMA 4500M (Anton-Paar) according to ASTM 4052 (2016) method at 15°C.

#### 2.3.5 Stability

The stability is evaluated by observing the changes in bio-oil viscosity throughout storage. The thermal treatment at 80 °C was applied for 24, 48, 72, and 96 h. After the accelerated aging procedure, it is possible to calculate these two parameters: stability index (SI) (Eq. (1)) and aging rate (AR) (Eq. (2)) (Pidtsang et al., 2016).

$$SI = \frac{V_{aged} - V_{fresh}}{V_{fresh}} \quad (1)$$

$$AR = \frac{V_{aged} - V_{fresh}}{96} \text{ (cSt/h)} \quad (2)$$

$V_{aged}$  and  $V_{fresh}$  are the average kinematic viscosity of aged and fresh HBO and mixtures samples. High SI values indicate low stability.

### 2.3.6 FT-IR

The FT-IR analysis identified the main chemical groups present in the heavy bio-oil phase and the heavy bio-oil phase with its solvent mixtures, which used the IR spectrophotometer Spectrum 100, Perkin Elmer, 550–4000  $\text{cm}^{-1}$ , resolution 32  $\text{cm}^{-1}$ , direct transmittance mode (ATR).

## 3. Results and Discussion

### 3.1 Effect of solvents on bio-oil heavy fraction stability

The selected solvents methanol, ethanol, and acetone could easily mix with the HBO, producing homogeneous solutions.

#### 3.2.1 Viscosity and stability

Table 1 shows the properties that characterize the stability of bio-oil heavy fraction and mixtures.

Table 1: Properties of bio-oil heavy fraction stability

Sample	Viscosity (cSt)					SI* <sub>(24h)</sub>	AR* (cSt/h)
	Aging time (h)	0	24	48	72		
Pure HBO		372.52 ± 0.88	938.32 ± 0.79	1,735.10 ± 0.94	2,142.75 ± 1.03	3,481.10 ± 1.37	1.52 32.38
10–M		55.58 ± 0.05	85.78 ± 0.05	129.49 ± 0.04	133.70 ± 0.11	147.99 ± 0.10	0.54 0.96
15–M		32.08 ± 0.08	42.19 ± 0.10	70.51 ± 0.03	79.33 ± 0.09	92.79 ± 0.12	0.31 0.63
10–E		70.39 ± 0.06	103.68 ± 0.09	135.31 ± 0.12	146.63 ± 0.08	151.58 ± 0.05	0.47 0.85
15–E		42.40 ± 0.01	52.42 ± 0.06	73.59 ± 0.10	84.72 ± 0.12	96.38 ± 0.08	0.24 0.56
10–A		67.53 ± 0.03	112.58 ± 0.05	165.56 ± 0.02	183.86 ± 0.08	203.09 ± 0.11	0.67 1.41
15–A		38.88 ± 0.03	62.79 ± 0.04	113.59 ± 0.02	131.64 ± 0.06	145.03 ± 0.12	0.62 1.11

\*Calculated from average kinematic viscosity (Equations 1 and 2).

The results indicate that the solvents physically diluted the pure HBO because the mixtures have much lower initial viscosities than the pure fraction. The initial viscosity of pure HBO is above 125 cSt, so it does not comply with the maximum value established by ASTM D7544 (2017). All samples at 0 and 24 h aged mixtures met the norm. Therefore, the three solvents could decrease initial HBO viscosity and improve its stability.

The performance of solvents varies according to its mass concentration in HBO. It was observed that 15 wt. % proportion achieved better results than 10 wt. %. The results showed that adding 15 wt. % of methanol in HBO, initial viscosity decreases about 11.6 times, reaching the lowest value for this property.

Figure 1 demonstrates that all mixtures had the same behavior: viscosity increases during the accelerated aging time. Even so, as the time of aging increases, the difference among the action of the solvents on HBO viscosity became more significant.

Methanol appeared to be much better than acetone and slightly more efficient than ethanol. These solvent actions in terms of reduction of bio-oil viscosity have been reported in previous studies (Mei et al., 2019); (Pidtsang et al., 2016); (Pidtsang et al., 2013); (Oasmaa et al. 2004); (Liu et al., 2014); (Udomsap et al., 2012). Then, these current results upgrading the bio-oil heavy fraction support this conclusion.

The Stability Index (SI), which evaluates changes of viscosity after aging in comparison to initial viscosity, was calculated for each sample. Figure 2 exhibits the SI trend to augment with aging time.

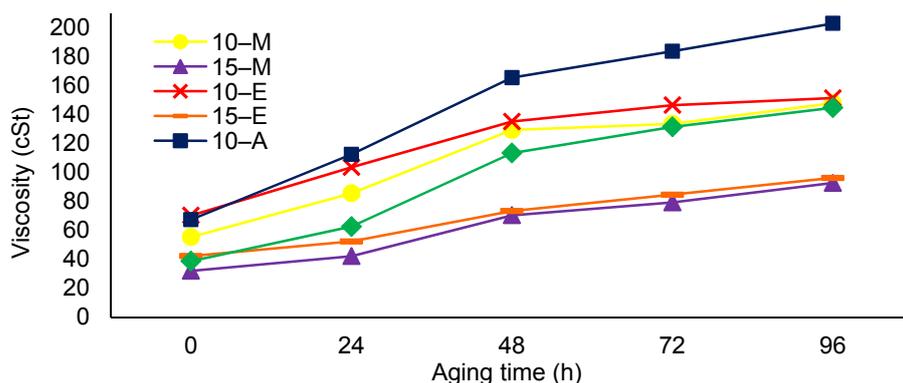


Figure 1: Viscosity variation of mixtures during accelerated aging

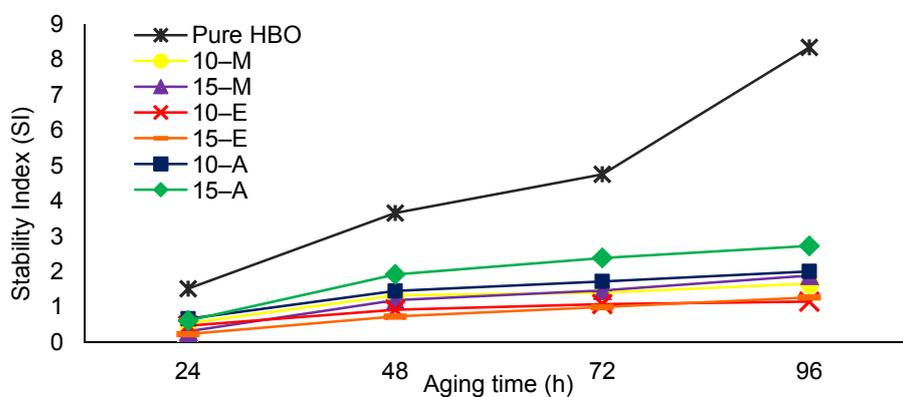


Figure 2: Stability Index (SI) variation during accelerated aging

The pure HBO had the highest SI, which indicates that when the solvent was added to this fraction, the stability could be improved. The sample 15-M, along with total aging time, seems to have the best stability. However, when evaluating only the first 24 hours, 15-E has the lowest SI value: 0.24 (Table 1). It demonstrates that ethanol could be as appropriate as methanol in terms of enhancing stability. Besides that, ethanol deserves a highlight for being from renewable sources and not as toxic as methanol.

The aging rate (AR), which is the other parameter used to compare stability, was also calculated. Table 1 shows that the AR of the pure bio-oil heavy fraction decreased from 32.38 cSt/h to 0.56–1.41 cSt/h when 10–15 wt. % of the solvent was added. The sample 15-E achieved the lowest AR value. It indicates that ethanol could be an acceptable choice due to its performance and green source. Also, ethanol can enhance bio-oil heating value (Pidtsang et al., 2013).

### 3.2.2 Water content, pH, and density

The solvent addition could decrease the initial water content of pure HBO, possibly by physical dilution (Table 2). After the 24 h accelerated aging procedure, the water content increased for all samples. This behavior has been reported by other authors (Mei et al., 2019); (Liu et al., 2014). The presence of water on bio-oil highly reduces its heating value (Oasmaa et al., 2015), being essential to lower the water content. The aged mixture samples also present lower values than aged pure HBO. Ethanol was more effective, reducing the initial water content of HBO from 13.43 % to 11.18 and 10.67 %, with 10 and 15 wt. %, respectively. The 10-M had higher water content among the aging mixtures. Reactions such as esterification and acetalization could occur between ethanol or methanol and HBO components and form water as a byproduct (Mei et al., 2019); (Oasmaa; Czernik, 1999).

The pH value of pure HBO decreased after 24 h aging. Table 2 shows that, compared to the pure HBO, the pH value of the initial and aged treatment group increased. Acetone was the least capable of enhancing pH value. Liu et al. (2014) reported that acetone could not prevent the acidification trend during storage. Two mechanisms can impact the pH value of bio-oil: the neutral dilution action of the solvent and the inhibition of  $H^+$  activity by the solvent (Liu et al., 2014); (Oasmaa et al., 2004).

Table 2: Water content, pH, and the density of pure HBO and its mixtures with solvents

Sample	Water Content (%)		pH		Density (kg/dm <sup>3</sup> )*	
	Fresh	Aged (24h)	Fresh	Aged (24h)	Fresh	Aged (24h)
Pure HBO	13.43 ± 0.36	13.64 ± 0.33	2.95 ± 0.01	2.66 ± 0.02	1.25	1.27
10-M	11.36 ± 0.14	13.37 ± 0.18	3.23 ± 0.03	3.25 ± 0.01	1.20	1.21
15-M	10.89 ± 0.10	12.76 ± 0.10	3.49 ± 0.04	3.41 ± 0.05	1.17	1.18
10-E	11.18 ± 0.07	13.28 ± 0.16	3.23 ± 0.04	3.09 ± 0.01	1.20	1.21
15-E	10.67 ± 0.09	12.61 ± 0.07	3.34 ± 0.02	3.22 ± 0.04	1.17	1.17
10-A	11.80 ± 0.04	12.88 ± 0.14	3.05 ± 0.01	2.91 ± 0.03	1.20	1.22
15-A	11.12 ± 0.15	12.39 ± 0.18	3.21 ± 0.02	3.01 ± 0.01	1.18	1.19

\*There was no significant standard deviation.

The density results suggest that all solvents in both mass concentrations could reduce their values. They also slightly increased for all samples after 24 h aging at 80 °C. Fresh and aged samples conform to the typical bio-oil density values found in the literature: 1.1 – 1.3 kg/dm<sup>3</sup> at 15 °C (Oasmaa et al., 2015).

### 3.2.3 FT-IR

The FT-IR spectra of the bio-oil heavy phase produced from bio-oil heavy fraction and of its solvent additions: 15 wt. % of methanol, 15 wt. % of acetone, and 15 wt. % ethanol are given in Figure 1.

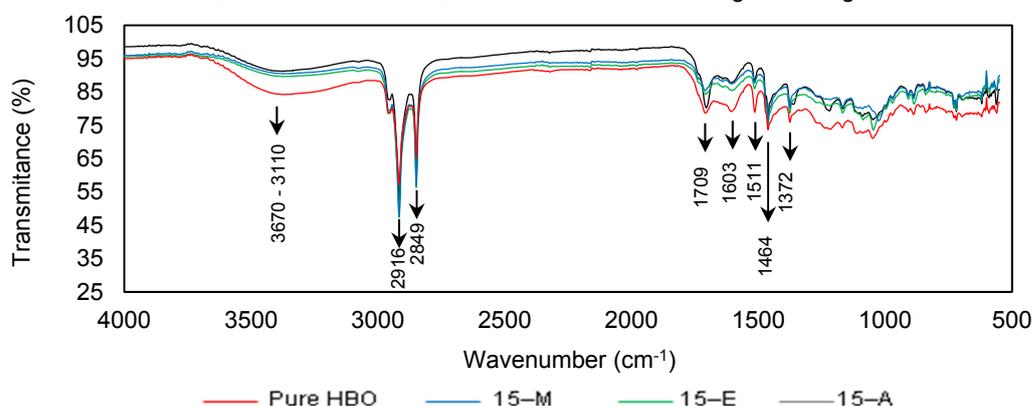


Figure 1. FT-IR spectra of the bio-oil heavy phase from sugarcane bagasse and the bio-oil heavy phase with solvent additions: acetone, ethanol, and methanol

The peaks below 1372 cm<sup>-1</sup> can indicate stretching vibrations of C–O from alcohols, esters, carboxylic acids, ethers, ketones, phenols, or aldehydes (Ozçimen and Karaosmanoglu, 2004); (Lin et al., 2016). The peak at 1372 cm<sup>-1</sup> can be symmetric vibration of C–H–(CH<sub>3</sub>). Also, the peak at 1464 cm<sup>-1</sup> can be related to C–H–(CH<sub>3</sub>) with symmetric vibration or C–H–(CH<sub>2</sub>) with asymmetric vibration (Lin et al., 2016). The peaks between 1511 and 1603 cm<sup>-1</sup> can refer to C=C stretching vibrations (Ozçimen and Karaosmanoglu, 2004); (Tsai et al., 2006) or even C–C in rings (Lin et al., 2016). The presence of a peak in 1709 cm<sup>-1</sup> could point to the C=O (ester) stretching vibration (Ozçimen and Karaosmanoglu, 2004); (Lin et al., 2016). The peaks at 2849 and 2916 cm<sup>-1</sup> demonstrate the C–H stretching vibration from aliphatic and olefinic, respectively (Ozçimen and Karaosmanoglu, 2004); (Lin et al., 2016). The peaks between 3670 and 3110 cm<sup>-1</sup> can evidence the presence of dimeric or polymeric O–H stretching vibrations from alcohols and water (Ozçimen and Karaosmanoglu, 2004); (Lin et al., 2016). The results show a slight displacement of adsorption peaks with solvent addition in bio-oil heavy fraction, which suggests that substitution reactions may have occurred between solvent and pure HBO components (Liu et al., 2014).

## 4. Conclusion

Sugarcane bagasse bio-oil heavy fraction was upgraded by solvent addition. Initially, HBO did not comply with the viscosity specification of ASTM D7544 (2017) for fast pyrolysis bio-oil. The pH and stability were enhanced, and viscosity and water content were reduced with the addition of methanol, ethanol and acetone. The effect of solvents was immediate and was maintained during the accelerated aging procedure at 80 °C. The higher the solvent content, the higher the improvement. Methanol and ethanol had nearly the same results of stability and could significantly decrease the aging rate. These two solvents, at 15 wt.%

concentration in HBO, could maintain the viscosity below the specification (maximum 125 cSt) after total aging time, which represents four years of storage. Acetone could improve the initial properties of HBO, but it could not inhibit the acidification trend. A more-depth statistical analysis (e.g. Pareto charts, surface area, effects table, etc.) can be done in future work. FT-IR results showed that solvent addition displaced the absorption peaks. It may indicate that substitution reactions occurred on the bio-oil heavy fraction.

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