

# Experimental Densities and Speeds of Sound of Substituted Phenols and Their Modeling with the Prigogine–Flory–Patterson Model

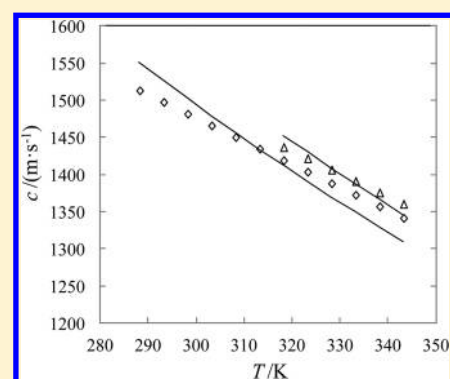
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**ABSTRACT:** This work provides new experimental data of speed of sound and density for seven pure components of pyrolysis bio-oil at atmospheric pressure for several phenols (phenol, *o*-, *m*-, and *p*-cresol), two phenolic ethers (2-methoxyphenol and eugenol) and one phenolic ester (methyl salicylate) at temperatures of (288.15 to 343.15) K. Densities and sound velocities are correlated with the Prigogine–Flory–Patterson (PFP) model. The properties are well described with the PFP model showing a better performance for the denser substances. The relation between density and speed of sound evidence the complex thermophysical behavior of substituted phenols.



## 1. INTRODUCTION

Beginning in the 1970s, with the petrol crisis, the importance of biofuels rose in science and technology, thus resulting in ethanol generated from sugar cane. Biofuels are defined as fuels produced from biological (biomass) and renewable sources, emerging as an alternative to fossil fuels, that contribute to the reduction of global warming, minimizing the generation of greenhouse gases and those harmful to the ozone layer.<sup>1,2</sup> The energy scenario for the next decades points to an increase in the use of biofuels, especially those produced from agricultural and industrial waste (second generation biofuels). The World Energy Council<sup>3</sup> estimates that, by 2050, the second generation biofuels may contribute approximately 40% of all transport liquid fuels. Bio-oil has begun to excel in this class, and its use is expected to expand rapidly throughout the world.

Fast pyrolysis is the most used process to produce this oil whose physical and chemical properties basically depend on the type of feedstock and the type of reactor for thermal decomposition.<sup>4,5</sup> Pyrolysis bio-oil is a complex mixture involving more than 300 compounds of which we highlight the phenols, phenolic ethers, and other oxygenated compounds.<sup>6–15</sup>

The growing interest in pyrolysis bio-oil has driven research in the thermophysical properties of these compounds. The speed of sound and isentropic compressibility have an important impact on the injection process. The latter affects the speed of pressure rise that will occur from the fuel pump pulse. The speed of sound in fuels affects pressure transmission speed through the injection line; therefore, as a consequence of

its higher speed of sound, blends with pyrolysis bio-oil propagate faster toward the injectors than petroleum fuels, resulting in an advance in fuel injection timing.<sup>16</sup> Injection timing advance can lead to earlier start of combustion, which raises peak in-cylinder temperature, thereby increasing thermal formation of NO.<sup>17</sup> The compressibility and speed of sound data are thus valuable information for system modeling and for experimental injection rate determination.<sup>18</sup>

In this work, experimental density,  $\rho$ , and speed of sound,  $c$ , data are reported at the temperature range (288.15 to 343.43) K and atmospheric pressure for the phenolic compounds commonly present in the fast pyrolysis bio-oil, that is, phenol, *o*-, *m*-, and *p*-cresol, 2-methoxyphenol, eugenol, and methyl salicylate. Density and speed of sound data were used to estimate Prigogine–Flory–Patterson (PFP)<sup>19,20</sup> model parameters, allowing the correlation of pure component thermophysical properties and aiming at developing models for the description of biofuels.

## 2. EXPERIMENTAL SECTION

The chemical substances studied in this work, their respective suppliers, purities, temperature range analyzed, and melting point are shown in Table 1.

The density and speed of sound were obtained using an automatic digital densimeter (Anton Paar DSA 5000). The

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**Table 1. Source and Purity for Each Substance Used in This Work**

chemical name	source	purity (100 w) <sup>a</sup>	temperature range (K) <sup>b</sup>	melting point (K) <sup>a</sup>
phenol	Bioquimís Científica	> 99	318.15 to 343.15	313.65
<i>o</i> -cresol	Bioquimís Científica	> 99	293.15 to 343.15	304.15
<i>m</i> -cresol	Bioquimís Científica	> 99	293.15 to 343.15	281.15 to 285.15
<i>p</i> -cresol	Bioquimís Científica	> 98	293.15 to 343.15	305.15 to 307.15
2-methoxyphenol	VE TEC	> 99	288.15 to 343.15	301.15 to 305.15
eugenol	VE TEC	> 99	288.15 to 343.15	263.95
methyl salicylate	Bioquimís Científica	> 99	288.15 to 343.15	265.15

<sup>a</sup>As informed by the supplier. <sup>b</sup>Temperature range in which data were obtained.

DSA 5000 simultaneously determines two physically independent properties within one sample.

The instrument is equipped with a density cell and a speed of sound cell. To determine density the known oscillating U-tube method is used. This method is based on the law of harmonic oscillation in which a U-tube filled with sample to be analyzed is subjected to an electromagnetic force. By measuring the frequency and period of vibration of the set the density of the sample is determined. This method gives very accurate measurements for this propriety.<sup>21</sup> For measurements of the speed of sound, the equipment has a stainless steel cell and uses the technique of pulse-echo, which refers to the transmission of a short pulse of ultrasound through the middle. When an obstacle is encountered, part of the pulse is reflected and the other part is transmitted. Thus, the equipment stores the time between the emission of the pulse and receiving the echo, turning it into distance.<sup>22</sup>

The density and speed of sound meter was calibrated against ultrapure water and air at atmospheric pressure. The calibration was accepted if the measurements were estimated to be within  $\pm 2 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  and  $\pm 0.02 \text{ m} \cdot \text{s}^{-1}$  of the reference values.

The standard uncertainty in the temperature is 0.01 K. The experimental uncertainties, obtained as described elsewhere,<sup>21</sup> were  $7 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$  and  $0.2 \text{ m} \cdot \text{s}^{-1}$ , for density and speed of sound, respectively.

### 3. RESULTS AND DISCUSSION

Experimental density and speed of sound data were measured for two phenolic ethers, 2-methoxyphenol and eugenol, and one phenolic ester, methyl salicylate. Furthermore, measurements for the four phenolic compounds, phenol, *o*-, *m*-, and *p*-cresol, were carried out at a narrower temperature range; that is, for phenol and *m*-cresol, measurements were only carried out above their melting points while, for *o*- and *p*-cresol and 2-methoxyphenol, measurements at metastable liquid temperature range (below their fusion temperature) were also included. Results of the density and speed of sound measurements for the studied compounds are listed in Table 2. A comparison between pure components properties obtained in this work and literature data is also presented in Table 2. Because of the relative lack of data at the highest temperatures of this work, the few data available up to temperatures higher than the studied here were interpolated to the temperatures of interest using a parabola. The interpolated data

are indicated in Table 2 and truncated up to the uncertainty of the original data. The measurements here reported are in very good agreement with those previously reported in the literature.

The density ( $\rho$ ) and speed of sound ( $c$ ) can be related with isentropic compressibility<sup>23</sup> ( $k_s$ ) as follows:

$$k_s = 1/(c^2\rho) \quad (1)$$

Table 2 also shows the isentropic compressibility calculated from the experimental data obtained in this work. Moreover, this property is used to calculate other thermodynamic properties, such as: isothermal compressibility ( $k_T$ ), thermal expansion coefficient ( $\alpha$ ), specific isobaric heat capacity ( $C_p$ ), temperature ( $T$ ), pressure ( $P$ ) and volume ( $V$ ), as presented in eqs 2 to 4.<sup>21,24</sup>

$$k_s = k_T - \alpha^2 T / (\rho C_p) \quad (2)$$

$$k_T = -1/V(\partial V/\partial P)_T \quad (3)$$

$$\alpha = 1/V(\partial V/\partial T)_p \quad (4)$$

In addition, as performed in our previous papers,<sup>21,25</sup> experimental density and speed of sound have been correlated by Prigogine–Flory–Patterson (PFP) model. According to this model, an equation of state is applicable in reduced form to pure liquids and mixtures:

$$\tilde{p}\tilde{V}/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1) - 1/(\tilde{V}\tilde{T}) \quad (5)$$

The reduced quantities are defined as

$$\tilde{p} = p/p^*, \quad \tilde{T} = T/T^*, \quad \text{and} \quad \tilde{V} = V/V^* \quad (6)$$

where  $p^*$ ,  $T^*$ , and  $V^*$  are characteristic parameters.

The method of weighted least-squares has been used to fit the values of the characteristic parameters for pure components, and details are presented in a previous paper.<sup>25</sup> PFP characteristic parameters for each substance were fitted in order to minimize the following objective function:

$$F_{\text{obj}} = \sum_{i=1}^n \{ [(\rho_i^{\text{calc}} - \rho_i^{\text{exp}})/\delta\rho]^2 + [(c_i^{\text{calc}} - c_i^{\text{exp}})/\delta c]^2 \} \quad (7)$$

where  $i$  indicates an experimental point,  $n$  indicates the number of experimental points, superscripts calc and exp stand for calculated and experimental, respectively, and  $\delta$  means the experimental uncertainty for pure substances. Initial guesses for these parameters were obtained as described elsewhere.<sup>26</sup>

Figures 1 and 2 show experimental and PFP results of densities and speeds of sound versus temperature for the studied compounds. It is worth noting that the error bars representing the confidence interval of uncertainty were not inserted because their size is smaller than the symbols used to denote the experimental measurements. As one can see, the PFP model correlates density very well, while the derivative of the speed of sound with respect to temperature is overestimated.

Additionally, the PFP model parameters are presented in Table 3.

As can be seen in Table 3, the characteristic volume parameter of the PFP model increases with increasing size of the molecule analyzed. A comparison of the phenol with cresol isomers shows that an average increase of about 14 units can be observed; that value represents the addition of a methyl ( $-\text{CH}_3$ ) in the structure of the molecule. In a comparison of

Table 2. Density,  $\rho$ , Speed of Sound,  $c$ , and Isentropic Compressibility,  $k_s$ , Data at (288.15 to 343.15) K, Obtained in this Work and from Literature When It Is Available<sup>a</sup>

T (K)	$10^{-3}\rho/(\text{kg m}^{-3})$		$c/(\text{m s}^{-1})$		$k_s/\text{TPa}^{-1}$	T (K)	$10^{-3}\rho/(\text{kg m}^{-3})$		$c/(\text{m s}^{-1})$		$k_s/\text{TPa}^{-1}$
	this work	literature	this work	literature	this work		this work	literature	this work	literature	this work
Phenol						<i>m</i> -Cresol					
318.15	1.054097	1.05331 <sup>27b</sup> 1.05435 <sup>29</sup>	1437.19	1440 <sup>28</sup>	459.36	303.15	1.025959	1.0261 <sup>38</sup> 1.0258 <sup>39</sup> 1.0260 <sup>50</sup>	1466.16	1465 <sup>38</sup> 1464.21 <sup>39</sup>	453.43
323.15	1.049814	1.0497 <sup>30</sup> 1.050 <sup>31</sup> 1.0499 <sup>33</sup> 1.0499 <sup>34</sup>	1422.09		471.09	308.15	1.021988	1.0221 <sup>38</sup> 1.0215 <sup>39</sup> 1.02164 <sup>52</sup> 1.0221 <sup>50</sup>	1450.55	1450 <sup>38</sup> 1449.27 <sup>39</sup>	465.04
328.15	1.045499		1406.77		483.34	313.15	1.017999	1.0170 <sup>39</sup> 1.018064 <sup>35</sup> 1.0160 <sup>40</sup> 1.01763 <sup>52</sup> 1.0181 <sup>50</sup> 1.0184 <sup>43</sup>	1434.97	1436.32 <sup>39</sup> 1434.20 <sup>35</sup>	477.05
333.15	1.041158	1.041 <sup>31</sup> 1.04101 <sup>32</sup> 1.0413 <sup>33</sup>	1391.42		496.10	318.15	1.013993	1.0135 <sup>39</sup> 1.01360 <sup>52</sup> 1.0141 <sup>50</sup> 1.0065 <sup>51</sup>	1419.45	1424.21 <sup>39</sup>	489.47
338.15	1.036792		1376.06		509.33	323.15	1.009965	1.0077 <sup>40</sup> 1.0098 <sup>49</sup> 1.00956 <sup>52</sup> 1.0102 <sup>45</sup>	1403.91		502.36
343.15	1.032398	1.033 <sup>31</sup> 1.0325 <sup>33</sup> 1.0328 <sup>34</sup>	1360.57		523.14	328.15	1.005910	1.0061 <sup>45c</sup>	1388.40		515.72
<i>o</i> -Cresol						333.15	1.001842	1.0004 <sup>40</sup> 1.0021 <sup>53</sup> 1.00144 <sup>52</sup> 1.0021 <sup>45c</sup>	1372.86		529.60
293.15	1.045771	1.045688 <sup>35</sup> 1.046 <sup>36</sup> 1.046 <sup>37</sup>	1522.59	1521.83 <sup>35</sup>	412.47	338.15	0.997743	0.9979 <sup>51</sup> 1.9980 <sup>45c</sup>	1357.32		544.03
298.15	1.041409	1.0423 <sup>38</sup>	1505.46	1505 <sup>38</sup> 1506 <sup>36</sup>	423.68	343.15	0.993626	0.99133 <sup>52</sup> 0.9940 <sup>45c</sup>	1341.83		558.96
303.15	1.037046	1.0369 <sup>38</sup> 1.0362 <sup>39</sup>	1488.19	1487 <sup>38</sup> 1485.26 <sup>39</sup>	435.40	<i>p</i> -Cresol					
308.15	1.032642	1.0316 <sup>38</sup> 1.0310 <sup>39</sup> 1.03273 <sup>41</sup> 1.03273 <sup>42</sup>	1470.21	1470 <sup>38</sup> 1466.84 <sup>39</sup>	448.01	293.15	1.034087	1.033994 <sup>35</sup> 1.0347 <sup>45</sup>	1502.88	1502.19 <sup>35</sup>	428.15
313.15	1.028246	1.0260 <sup>39</sup> 1.028145 <sup>35</sup> 1.0260 <sup>40</sup> 1.0290 <sup>43</sup> 1.0282 <sup>44</sup> 1.0280 <sup>45</sup>	1452.65	1452.11 <sup>39</sup> 1453.35 <sup>35</sup>	460.87	298.15	1.030253	1.0302 <sup>38</sup> 1.0295 <sup>45</sup>	1487.15	1486 <sup>38</sup>	438.88
318.15	1.023825	1.0211 <sup>39</sup> 1.02298 <sup>27b</sup>	1435.18	1437.06 <sup>39</sup>	474.20	303.15	1.026390	1.0263 <sup>38</sup> 1.0265 <sup>39</sup>	1471.38	1471 <sup>38</sup> 1468.43 <sup>39</sup>	450.03 461.57
323.15	1.019387	1.0174 <sup>40</sup> 1.0203 <sup>46</sup> 1.0198 <sup>45</sup>	1417.70		488.08	308.15	1.022504	1.0224 <sup>38</sup> 1.0220 <sup>39</sup> 1.0225 <sup>45</sup>	1455.63	1455 <sup>38</sup> 1455.79 <sup>39</sup>	
328.15	1.014933	1.019 <sup>47c</sup> 1.0154 <sup>45c</sup>	1400.25		502.52	313.15	1.018593	1.0181 <sup>39</sup> 1.018470 <sup>35</sup> 1.0188 <sup>41</sup> 1.0168 <sup>40</sup> 1.0186 <sup>43</sup>	1439.97	1443.68 <sup>39</sup> 1439.56 <sup>35</sup>	473.47
333.15	1.010461	1.0084 <sup>40</sup> 1.015 <sup>47c</sup> 1.0112 <sup>45c</sup>	1382.83		517.54	318.15	1.014661	1.0139 <sup>39</sup> 1.01401 <sup>27b</sup>	1424.29	1432.73 <sup>39</sup>	485.83
338.15	1.005972	1.011 <sup>47c</sup> 1.0070 <sup>45c</sup>	1365.31		533.28	323.15	1.010701	1.0092 <sup>40</sup> 1.0126 <sup>46</sup> 1.010 <sup>47c</sup> 1.0102 <sup>45</sup>	1408.66		498.61
343.15	1.001464	1.007 <sup>47c</sup> 1.0027 <sup>45c</sup>	1347.70		549.77	328.15	1.006716	1.006 <sup>47c</sup> 1.007 <sup>45c</sup>	1393.05		511.87
<i>m</i> -Cresol						333.15	1.002702	1.0017 <sup>40</sup> 1.002 <sup>47c</sup> 1.003 <sup>45c</sup>	1377.44		525.63
293.15	1.033835	1.033994 <sup>35</sup> 1.03385 <sup>41</sup> 1.03385 <sup>42</sup> 1.0341 <sup>45</sup>	1497.87	1496.76 <sup>35</sup>	431.14	338.15	0.998659	0.998 <sup>47c</sup>	1361.85		539.91
298.15	1.029907	1.0301 <sup>38</sup> 1.0275 <sup>48</sup> 1.0297 <sup>49</sup> 1.0299 <sup>50</sup> 1.0202 <sup>51</sup> 1.0300 <sup>45</sup>	1481.93	1481 <sup>38</sup>	442.13						

Table 2. continued

T (K)	$10^{-3}\rho/(\text{kg m}^{-3})$		$c/(\text{m s}^{-1})$		$k_s/\text{TPa}^{-1}$	T (K)	$10^{-3}\rho/(\text{kg m}^{-3})$		$c/(\text{m s}^{-1})$		$k_s/\text{TPa}^{-1}$
	this work	literature	this work	literature	this work		this work	literature	this work	literature	this work
<i>p</i> -Cresol						Eugenol					
		0.999 <sup>45c</sup>						1.05091 <sup>60</sup>			
343.15	0.994587	0.994 <sup>47c</sup>	1346.22		554.79	308.15	1.053211		1442.15		456.53
		0.995 <sup>45c</sup>				313.15	1.048784	1.04200 <sup>60</sup>	1424.07		470.17
2-Methoxyphenol						Methyl Salicylate					
288.15	1.138641	1.139 <sup>54</sup>	1567.56		357.41	318.15	1.044353		1406.08		484.32
293.15	1.133806	1.136 <sup>54</sup>	1548.28		367.93	323.15	1.039920		1388.22		498.98
298.15	1.128959	1.1289 <sup>56</sup>	1528.74		379.01	328.15	1.035483		1370.45		514.20
		1.132 <sup>54</sup>				333.15	1.031042	1.02408 <sup>60</sup>	1352.82		529.96
303.15	1.124107	1.129 <sup>54</sup>	1509.31		390.51	338.15	1.026602		1335.25		546.36
		1.124 <sup>47c</sup>				343.15	1.022153		1317.75		563.41
308.15	1.119248	1.126 <sup>54</sup>	1489.95		402.47						
		1.119 <sup>47c</sup>				288.15	1.189318	1.1890 <sup>54</sup>	1447.56		401.27
313.15	1.114383	1.123 <sup>54</sup>	1470.68		414.89			1.18890 <sup>63</sup>	1446.9 <sup>(63)</sup>		
		1.115 <sup>55</sup>				293.15	1.184327	1.1852 <sup>54</sup>	1429.11		413.42
		1.115 <sup>57</sup>						1.1838 <sup>59</sup>			
		1.114 <sup>47c</sup>				298.15	1.179336	1.1817 <sup>54</sup>	1410.63		426.13
318.15	1.109511	1.109 <sup>47c</sup>	1451.52		427.78			1.1782 <sup>64</sup>			
323.15	1.104630	1.104 <sup>47c</sup>	1432.41		441.21			1.1798 <sup>65</sup>			
328.15	1.099743	1.099 <sup>47c</sup>	1413.46		455.14	303.15	1.174350	1.17380 <sup>63</sup>	1392.27	1391.2 <sup>63</sup>	439.29
333.15	1.094844	1.079 <sup>55</sup>	1394.57		469.64			1.1729 <sup>66</sup>			
		1.094 <sup>47c</sup>						1.1753 <sup>67</sup>		1398.0 <sup>67</sup>	
338.15	1.089939	1.089 <sup>47c</sup>	1375.81		484.71	308.15	1.169367	1.1679 <sup>66</sup>	1374.05		452.94
343.15	1.085019	1.086 <sup>57</sup>	1357.08		500.44			1.167 <sup>47c</sup>			
		1.084 <sup>47c</sup>				313.15	1.164384	1.1629 <sup>66</sup>	1356.03		467.05
Eugenol						Eugenol					
288.15	1.070898	1.0696 <sup>58</sup>	1515.33		406.66	318.15	1.159405	1.1579 <sup>66</sup>	1338.11		481.70
293.15	1.066485	1.0667 <sup>59</sup>	1497.05		418.38			1.158 <sup>47c</sup>			
		1.0663 <sup>58</sup>				323.15	1.154425	1.153 <sup>47c</sup>	1320.36		496.88
		1.05984 <sup>60</sup>				328.15	1.149447	1.148 <sup>47c</sup>	1302.78		512.59
298.15	1.062062	1.0633 <sup>58</sup>	1478.65		430.64	333.15	1.144464	1.143 <sup>47c</sup>	1285.37		528.86
303.15	1.057638	1.060 <sup>61</sup>	1460.34		443.36	338.15	1.139475	1.139 <sup>47c</sup>	1268.07		545.77
		1.058 <sup>62</sup>				343.15	1.134488	1.134 <sup>47c</sup>	1250.88		563.34

<sup>a</sup>Standard uncertainty  $u$  is  $u(T) = 0.01$  K, and the combined expanded uncertainties  $U_c$  are  $U_c(\rho) = 0.014$  kg·m<sup>-3</sup>,  $U_c(c) = 0.40$  m·s<sup>-1</sup>, and  $U_c(k_s) = 0.28$  TPa<sup>-1</sup> (level of confidence = 0.95). <sup>b</sup>Density at 319.15 K. <sup>c</sup>Interpolated data.

the cresols to 2-methoxyphenol, a small increase in the value of the characteristic volume can be observed due to the addition of one oxygen atom. Considering eugenol, it has a larger characteristic volume than the 2-methoxyphenol, this increase corresponds to approximately three times the value of a methyl radical. However, for methyl salicylate this value is smaller than that of eugenol and greater than that of 2-methoxyphenol, due to a carboxyl radical.

Similarly, although not shown in the table, the value of the segment interaction energy, proportional to  $p^*(V^*)^2$ , also increases with the increase of molecule volume. The same occurs for the number of effective external degrees of freedom per segment, which is proportional to  $p^*V^*/T^*$ ; that is, the values of these parameters vary according to the increase of molecule size.

To evaluate the ability of the PFP model, the root-mean-square-deviations (RMSD) were calculated, as shown in eq 8, where  $w$  represents each property studied and  $n$  is the number of systems studied. Absolute relative deviations (AD) between correlated and experimental values of density and speed of sound and the corresponding average absolute relative deviation (AAD) were also calculated to evaluate this model using eqs 9 and 10.

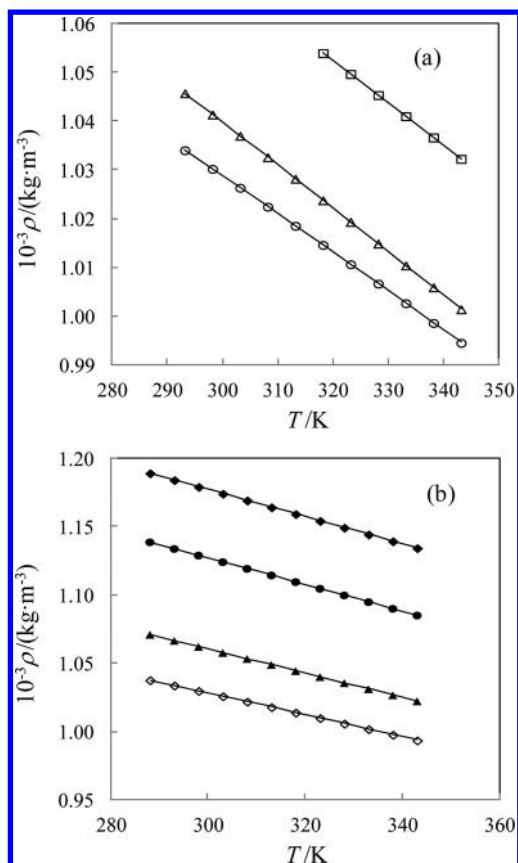
$$\text{RMSD} = \sqrt{\frac{\sum_{i=1}^n (w_i^{\text{exp}} - w_i^{\text{calc}})^2}{n}} \quad (8)$$

$$\text{AD}_i(\%) = \left| \frac{w_i^{\text{calc}} - w_i^{\text{exp}}}{w_i^{\text{exp}}} \right| 100 \quad (9)$$

$$\text{AAD}(\%) = \frac{\sum_{i=1}^n \text{AD}_i}{n} \quad (10)$$

RMSD and AAD deviations for density and speed of sound for each studied compound class are presented in Table 4. As shown here the PFP model provides a good description of the density and speed of sound for all studied compounds. At lower temperatures, the PFP model overestimates the speed of sound data with deviations higher than its experimental uncertainty, while the opposite trend is observed at higher temperatures. The same trends were observed previously when density and speed of sound of tetralin, *n*-decane, *n*-dodecane, and *n*-hexadecane were correlated, although the deviations on the derivative of speed of sound with respect to temperature were less pronounced for these substances.<sup>21,25</sup> This suggests that the polar groups present in the substances studied in this work make the description of the speed of sound by the PFP model more difficult.

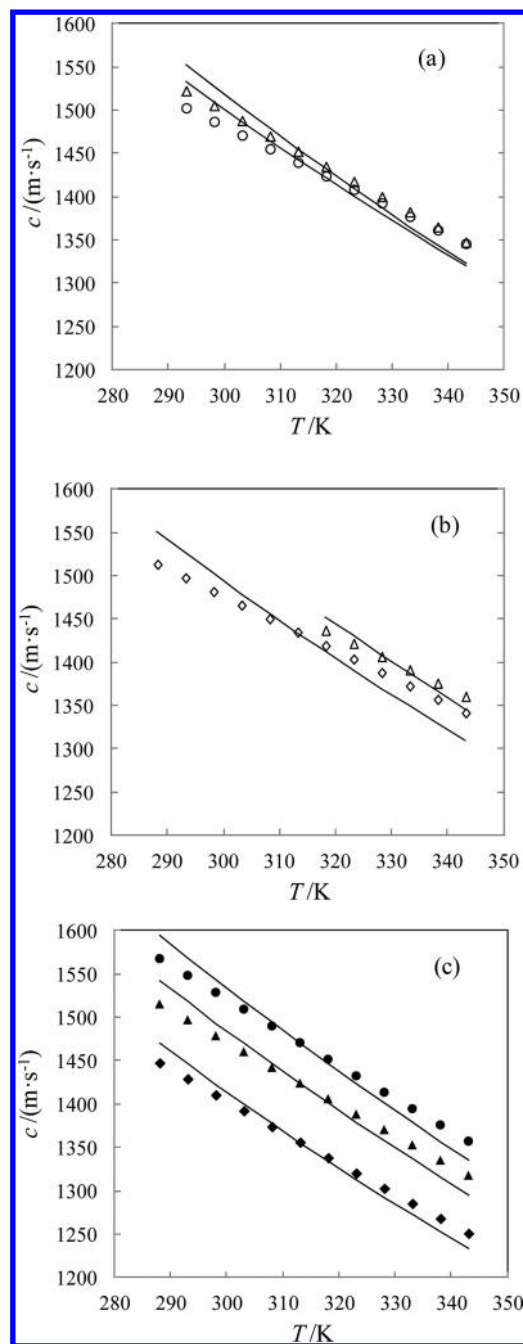
This ensemble of results allows the analysis of the effect of side groups in the phenol molecular structure, which was used as reference, on the density and speed of sound. It is generally



**Figure 1.** Effect of temperature,  $T$ , upon densities, (a) for  $\Delta$ , *o*-cresol and  $\circ$ , *p*-cresol and  $\square$ , phenol; (b) for  $\diamond$ , *m*-cresol; for  $\bullet$ , 2-methoxyphenol, and  $\blacktriangle$ , eugenol; and for  $\blacklozenge$ , methyl salicylate. Solid lines have been calculated from PFP model.

known that these properties are functions of molecular length and shape, and intermolecular interactions, that draw the molecular arrangement into the liquid phase.<sup>21,25</sup> Speed of sound and density are inversely related to compressibility. It is thus expected that higher densities lead to lower compressibility or higher speeds of sound. This tendency was observed when the density and speed of sound values of phenol, cresols, and 2-methoxyphenol were compared. The results show that the phenol compounds become less dense when a side methyl group is bonded to the aromatic ring. This could be attributed to the decrease in the polar character of the molecule, weakening the intermolecular interaction energy. When, instead, an ether group is bonded at the ortho position, as observed on 2-methoxyphenol, density and speed of sound values increase in comparison with those of the phenol, lowering the compressibility. This inversion in behavior should be attributed to the polar interactions between hydroxyl and ether groups.

An analysis of the change from 2-methoxyphenol to eugenol shows, again, that the weakening in intermolecular interaction energy caused by the decrease in polar character diminishes density and speed of sound, and enlarges compressibility. However, this was not observed when there was a change from phenol or 2-methoxyphenol to methyl salicylate, which led to an increase in density but decrease in speed of sound and increase in compressibility. This result further evidences the complex behavior of these systems. Furthermore, it is noteworthy that as temperature increases, not only the



**Figure 2.** Effect of temperature,  $T$ , upon speed of sound (a) for  $\Delta$ , *o*-cresol and  $\circ$ , *p*-cresol; (b) for  $\diamond$ , *m*-cresol and  $\square$ , phenol; (c) for  $\bullet$ , 2-methoxyphenol and  $\blacktriangle$ , eugenol; and for  $\blacklozenge$ , methyl salicylate. Solid lines have been calculated from PFP model.

**Table 3. Parameters for the Prigogine–Flory–Patterson (PFP) Model**

substance	$P^*/\text{MPa}$	$10^6 V^*/(\text{m}^3 \text{mol}^{-1})$	$T^*/\text{K}$
phenol	718	73.29	6081
<i>o</i> -cresol	711	85.80	5850
<i>m</i> -cresol	634	87.80	6162
<i>p</i> -cresol	630	88.00	6228
2-methoxyphenol	753	90.60	5785
eugenol	630	128.00	5903
methyl salicylate	671	106.60	5856

**Table 4. RMSD and AAD for Density and Speed of Sound for PFP Model**

compound class	RMSD		AAD	
	$\rho/(\text{kg}\cdot\text{m}^{-3})$	$c/(\text{m}\cdot\text{s}^{-1})$	$\rho$ (%)	$c$ (%)
phenolic compounds	0.06	16.6	0.004	1.09
phenolic ethers	0.16	15.3	0.012	1.00
phenolic ester	0.20	12.5	0.015	0.80
global	0.12	15.7	0.009	0.98

properties for each compound decrease but also differences among the different compounds studied become less pronounced (Figures 1 and 2).

#### 4. CONCLUSIONS

Measurements of density and speed of sound were performed for seven pure components of pyrolysis bio-oil, which are four phenols, phenol, *o*-, *m*- and *p*-cresol, two phenolic ethers, 2-methoxyphenol and eugenol, and one phenolic ester, methyl salicylate, at atmospheric pressure and temperatures ranging from (288.15 to 343.15) K. The PFP model was used to correlate these data. Density data is well described by the model, while the derivative of speed of sound with respect to temperature is somewhat overestimated. The ability of the PFP model to correlate both properties was found for to be better for denser substances. Also, the relation between density and speed of sound evidence the complex thermophysical behavior of the substituted phenols.

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##### Notes

The authors declare no competing financial interest.

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