Gas and char formation from guaiacol as lignin model compound in sub- and supercritical water (SCW) was conducted in a continuous flow system for 300–450 °C and 25 MPa at short residence time of 0.5–40 s. Both char and gaseous formation are qualitatively and quantitatively determined to establish its yield and its formation trend with temperature and residence time. The high yields of CO₂, H₂, CH₄, and zero CO indicates that the gaseous compounds are produced from direct decompositions of guaiacol and its derivative compounds instead of reaction among gas species and water. On the other hand, there is significant higher yield of char in supercritical region. It is established that gas-forming reactions are competing with cross-linking between the reactive degradation fragments from the degraded lignin to form char.

A large portion of biomass contains high percentage of water, which causes high drying costs when classical gasification process is used. Therefore, hydrothermal gasification of biomass is a promising technology for high moisture content compounds. Lignin, a compound from biomass is an amorphous three-dimensional polymeric substances consisting of phenylpropane units and contains abundant aromatic rings with aliphatic groups in addition to hydroxyl and methoxyl substituents. Among all the compounds in biomass, lignin is the hardest to be converted into gaseous or liquid compounds.

Resende and Savage¹ reported that lignin can be gasified to produce H₂ and CH₄ under sub- and supercritical conditions. However, char formation is significantly enhanced especially under supercritical conditions, suppressing gaseous formation pathways. This is an interesting and important issue for biomass conversion in hydrothermal reaction because char is undesirable by-products and conversion to gas is preferable.

Therefore, the purpose of this study is to investigate char and gas formation from guaiacol under hydrothermal conditions and short residence time of 0.5–40 s. The short residence time allows us to investigate how fast char and gaseous compounds are formed. Guaiacol (o-methoxyphenol) is selected because it is the simplest model compound for lignin and has the important structural features of lignin. Guaiacol contains abundance of aromatic rings with hydroxyl and methoxyl substituents similar to lignin.

The schematic of the experimental apparatus is shown in Fig. 1. The reactor is made of SS316 steel tubing (ID: 1mm, OD: 1.59mm) of the length of 20 m. Guaiacol solution (0.5 wt%) is mixed with preheated water at the entrance point just before the reactor zone. This allows the solution heated to the reaction temperature instantaneously. The gaseous compounds are analyzed by gas chromatograph (GC). The solid product particles were trapped in the inline filter. These solid particles were subsequently removed and dried overnight and weighed until a constant weight was reached. Elemental analysis of char were performed on a Perkin Elmer Series II CHNS/O Analyzer 2400.

The concentration of guaiacol solution is 0.1 wt% at room temperature after mixing. Reaction pressure and temperature are 25 MPa and 300–450 °C, respectively. The residence time is 0.5–40 s.
3. Results and discussions

3.1 Char yield
Char formation from guaiacol conversion in hydrothermal conditions (Fig. 2) exhibits similar behavior with lignin. High char yield is obtained exclusively in supercritical region. In addition, char formation are observed within 2 s at these temperatures, which indicates rapid reaction. The cross-linking reaction between the active sites and the phenolic structures in large fragments could produce higher molecular weight fragments referred to as char. In addition, the formation of these high molecular weight fragments is important for guaiacol decomposition to reach equilibrium conditions. From LCMS analysis, multiple benzene ring constituents (2-phenoxybiphenyl and p-terphenyl) are observed only in supercritical region. This is an important indication of similar cross-linking reaction even within short residence time.

In supercritical conditions, pyrolysis are promoted to produce highly reactive radical intermediates through the fission of the weaker aliphatic C–O bond of the methoxyl group. These highly reactive radicals will then disproportionate and subsequently cross-linked to form higher molecular weight fragments corresponding to char.

3.2 Gas yield
The carbon gaseous yield obtained in this study is shown in Fig. 3. It is evident that the carbon gaseous yield from guaiacol is enhanced under near and supercritical conditions (420–450 °C). Gaseous yield are already observed within short residence time (0.5 s) indicative of rapid formations.

The main gaseous products from guaiacol gasification were H2, CO2, CH4 fractions are enhanced in supercritical temperatures. No CO are produced. The high H2, CO2, and CH4 formation but zero CO under supercritical condition even at short residence times indicates that the gaseous compounds are produced from the direct conversion of the liquid phase either from liquid products and/or from guaiacol itself. In addition, the similarity is also observed for hydrothermal gasification of lignin.

The kinetic analysis of guaiacol decomposition from the reaction network model as shown in Fig. 4 has been carried out.

Fig. 5 shows the Arrhenius plot with comparison to other studies. We obtained the pre-exponential factor of 116.69 s\(^{-1}\) and activation energy of 34.25 kJ/mol while Wahyudiono et al. obtained activation energy of 38.75 kJ/mol.

4. Conclusion
Char and gaseous yield from guaiacol decomposition under hydrothermal conditions have been determined. In addition, the decomposition behavior can be reasonably explained by the first-order kinetic model.

References