et al., 2000), and severity factor (Galbe and Zacchi, 2007) were considered to specify the procedures.

Table 2 represents the experimental data of the organosolv pretreatment process using three different catalysts conducted for selecting the conditions. Pretreated material yield of organosolv pretreatment with sulfuric acid was only about 60%, while that of the organosolv process with magnesium chloride was approximately 70%.

For the organosolv pretreatment with sulfuric acid, pretreatment at 180 °C for 0 min showed a superior performance with high pretreated material yield (61.5%), high digestibility (57.0%), high glucose yield (75.5%), low H-factor value (154.4), and low severity factor (1.4).

For the organosolv pretreatment with magnesium chloride, pretreatment at 210 °C for 10 min showed a better performance with higher pretreated material yield (69.5%), higher digestibility (61.2%), and higher glucose yield (75.8%) than the process at 200 °C for 20 min. H-factor from this process was slightly higher, but the severity factor was the same at 4.2.

In the organosolv pretreatment with 1% sodium hydroxide, digestibility of pretreated materials even at 210 °C for 20 min was very low at 20%. Accordingly, the organosolv pretreatment process with low sodium hydroxide concentration did not improve enzymatic digestibility even with high energy input. The organosolv process with a 2% concentration of sodium hydroxide (w/v) was carried out to improve enzymatic digestibility (Fig. 1c).

Enzymatic digestibility improved with higher concentration of sodium hydroxide. In the pretreatment with sodium hydroxide at 190 °C for 20 min, for example, digestibility of organosolv pretreated materials with 1% sodium hydroxide was only 12.0%, but that with 2% catalyst improved up to 58.0%. Digestibility of organosolv pretreated pitch pine with 2% sodium hydroxide was 85.4% at 210 °C for 20 min, which continuously improved, while pretreatment with sulfuric acid or magnesium chloride did not improve enzymatic digestibility even at the most severe condition. Nevertheless, pretreated material yields also decreased considerably in severe conditions, as shown in Fig. 1d. With respect to digestibility and pretreated material yield, pretreatment condition at 190 °C for 20 min was selected, obtaining 58.0% of digestibility and 58.8% of pretreated material yield, which were comparatively higher than the others are.

3.2. Cellulose-to-glucose conversion yield and theoretical ethanol yield at selected conditions

Cellulose-to-glucose conversion was compared by enzymatic hydrolysis for 72 h with the pretreated materials at their selected condition (Fig. 2a). Organosolv pretreatment with 1% sulfuric acid at 180 °C for 0 min, with 1% magnesium chloride at 210 °C for 10 min, and with 2% sodium hydroxide at 190 °C for 20 min was carried out for comparison; these conditions were selected as optimal conditions.

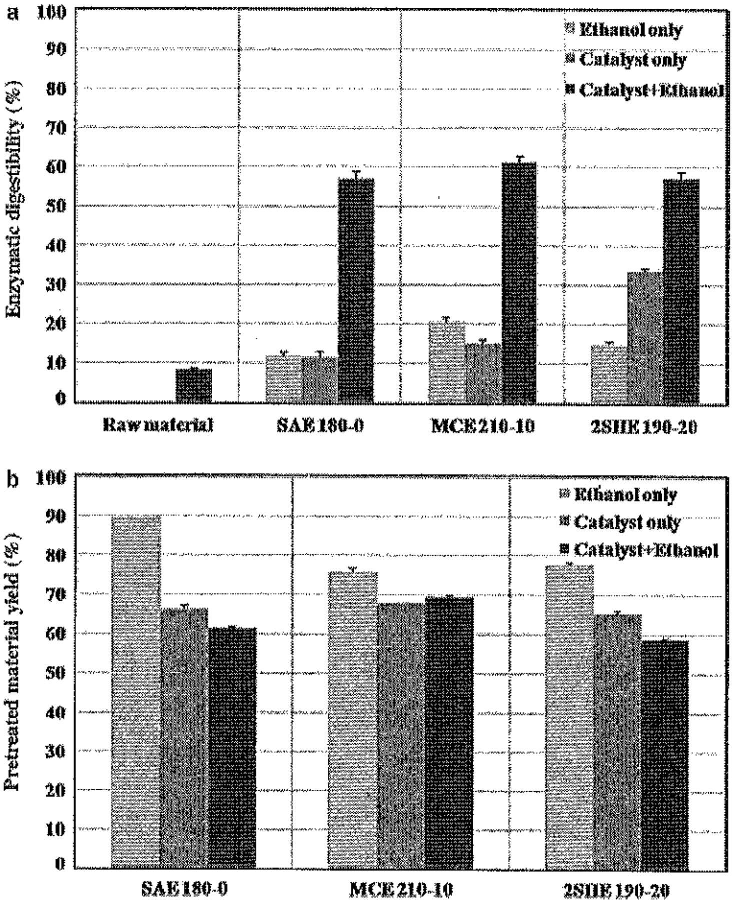

Fig. 3. Effects of catalysts and ethanol on (a) enzymatic digestibility, and (b) pretreated material yield. SAE 180-0, organosolv pretreatment with 1% sulfuric acid at 180 °C for 0 min; MCE 210-0, organosolv pretreatment with 1% magnesium chloride at 210 °C for 10 min; 2SHE 190-20, organosolv pretreatment with 2% sodium hydroxide at 190 °C for 20 min.

Low conversion of raw material showed that pitch pine was recalcitrant and difficult to convert even as wood powder, but organosolv pretreatment improved its enzymatic hydrolysis rate. Organosolv pretreated material with 1% sulfuric acid was converted the most rapidly with the highest conversion yield at nearly 93%. Organosolv pretreated material with 1% magnesium chloride was converted slower and had lower yield than that with sulfuric acid. Pretreated material with 2% sodium hydroxide converted the slowest, and the yield was also the lowest at 73%.

Ethanol production was carried out at each condition (Fig. 2b). Most ethanol was produced by *S. cerevisiae* in 24 h, and the amount slightly decreased because of the inhibitory effect of ethanol on yeast. Theoretical ethanol yield was the highest at 70% from pretreated material with sulfuric acid, while ethanol yield from pretreated materials with magnesium chloride and with 2% sodium hydroxide were comparatively low at 60% and 45%, respectively.

3.3. *Analysis for evaluating three different catalysts*

3.3.1. *Effects of catalysts and the organic solvent*

Pretreatment and the enzymatic hydrolysis process were conducted at selected pretreatment conditions. Materials were pretreated by 50% ethanol solution as the ethanol-control and by each catalyst solution without ethanol as the catalyst-control (Fig. 3a). Digestibility of ethanol-controls slightly increased as pretreatment conditions became more severe, but it did not achieve good efficiency, as did the organosolv process. The digestibility of catalyst-controls was low except in the case of 2% sodium hydroxide-control. The digestibility of 2% sodium hydroxide-control increased up to 33.6%, which means sodium hydroxide is a strong reagent. However, it was also not as effective as the organosolv process.

These results show that the catalyst and the solution do not act independently but instead act synergetically.

Fig. 3b represents the pretreated material yield after each pretreatment process. Of the pretreated material, 69.5% was obtained by organosolv pretreatment with 1% magnesium chloride as the highest yield, and 61.5% and 58.8% of pretreated material yield was obtained with 1% sulfuric acid and with 2% sodium hydroxide, respectively, as the relatively lower yield. Pretreated material yield of ethanol-controls was higher than that of catalyst-controls. Although pretreated material yield of acid or neutral catalyst-controls was similar to that of organosolv pretreated materials, enzymatic digestibility was much lower. This shows that acid or neutral catalysts can degrade some wood components such as hemicelluloses, but the degradation is not enough to enhance enzyme accessibility.

3.3.2. *Chemical composition of pretreated materials*

The chemical composition of pretreated materials considering their mass balance is presented in Fig. 4. For organosolv-treated materials with sulfuric acid or magnesium chloride, lignin contents seldom decreased at 23.78% and 25.78%, respectively, compared with 26.16% of raw materials. These results agree with the previous studies that the organosolv process using sulfuric acid and ethanol does not decrease lignin contents in biomass (Pan et al., 2007).

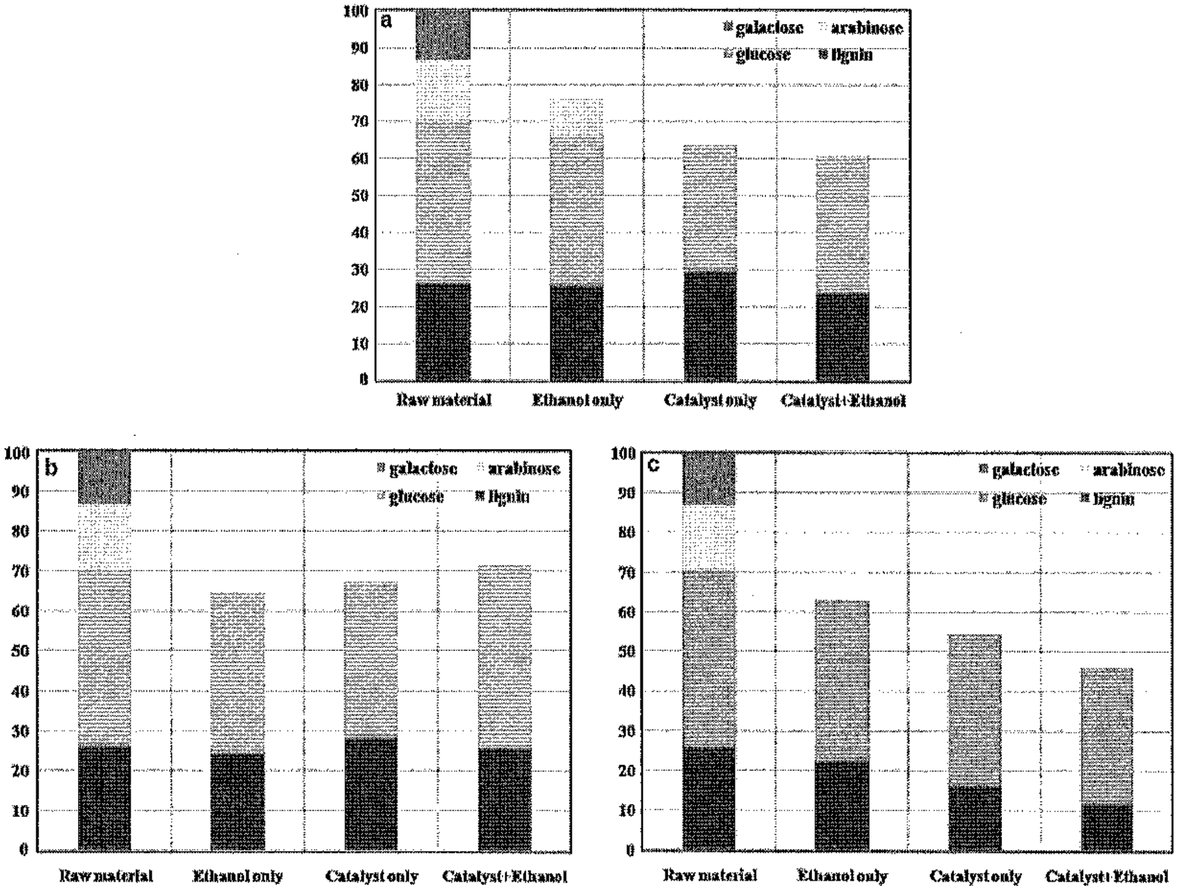

Fig. 4. Chemical composition of pretreated materials with (a) 1% sulfuric acid at 180 °C for 0 min, (b) 1% magnesium chloride at 210 °C for 10 min, and (c) 2% sodium hydroxide at 190 °C for 20 min.