Production of furfural from biomass has attracted many research interests due to its usefulness as important chemical solvent and chemical feedstock for value-added products. Conversion of D-xylose to furfural via dehydration reaction enhanced by heterogeneous catalyst has also been an interesting issue. In this work, single-walled carbon nanohorns (CNHs) hybridized with metal nanoparticles were proposed for catalytic dehydration of D-xylose to furfural for the first time. CNHs hybridized with Ni and Cu nanoparticles were in-house prepared by Gas-inject arc-in-water (GIAIW) and then used as a catalyst for D-xylose dehydration. Physical and chemical properties of the catalyst samples were investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD), thermogravimetric analyzer and BET analyzer. It is notable that Ni/CNHs provided the highest D-xylose conversion and furfural yield.

Key Words
Furfural, D-xylose, Dehydration, Carbon nanohorn, Catalyst, Nanoparticle

1. Introduction
At present, the global energy consumption has continuously increased while remaining reserve of fossil fuel is decreased. Also the global warming problem resulted from fossil fuel burning became an important issue for humanity. According to this situation, sustainable and friendly source of energy becomes an interesting research topic. Biomass is one of promising alternative sources, which can be converted into high value-added products including biofuel. Lignocellulose is the most abundantly available raw material, which is appropriate to use as a feedstock to produce alternative fuel and other valuable products. Furfural is a biomass-derived chemical which can be produced through dehydration of xylose. Furfural is typically used as an organic solvent or a chemical feedstock for biochemical and biofuel production. In existing commercial process, mineral acids (H₂SO₄ and HCl) have been used as Bronsted acids for the dehydration of xylose to furfural. However, the activity of the catalyst still low and this type of catalyst has several drawbacks, such as instrument corrosion, excessive waste disposal and high investment in catalyst recovery process. To overcome such problems, solid acid catalysts would be an alternative way for dehydration of xylose. Many research teams have paid attention on development of solid acid catalysts to improve the activity of the reaction by varying support material or functional groups on the support. Meanwhile, carbon-based catalyst with modified surface has also been examined because of their advantages in high thermal stability and high activity. In addition, it is known that carbon-based catalyst exerts a potential in water tolerance under high temperature which is preferable for hydrothermal reaction.
of the carbon-based nanostructural materials, which can be used as catalyst or catalyst support. Basically, the advantages of CNHs when compared to conventional carbon black or activated carbon are high oxidation stability due to their graphitic nanostructure and tunable porous structure which are promising for various applications. In addition, with appropriate synthesizing methods CNHs could be mass produced without dependence upon usage of metal catalysts when compared to SWCNTs or MWCNTs. Nevertheless, hybridization of such CNHs with other additive species could be achieved by various controllable methods. There are several alternative methods to produce high purity CNHs, such as CO2 laser ablation and arc discharge. However, among those alternatives gas-inject arc-in-water method (GI-AIW) is a simple and cost effective method for mass production of CNHs. There are many applications for CNHs, such as electronic electrode, biosensor, catalyst support and gas storage. Poonjarernsilp et al. (2014) reported that modified CNHs could provide satisfactory performance as an effective catalyst for novel hydrocarbon compound production. However, there is no report on usage of CNHs hybridized with NiCu alloy (NiCu/CNHs) as a catalyst for dehydration of D-xylose to furfural. Therefore main objective of this work was to examine synthesis of CNHs hybridized with Ni, Cu and NiCu alloy by GI-AIW route and catalytic performance of CNHs in dehydration of D-xylose for producing other high value-added products. Comparison of catalytic role of pristine CNHs, CNHs hybridized with Ni, Cu and Ni/Cu alloy was investigated and discussed with respect to difference in conversion of D-xylose and yield of furfural.

2. Experimental

Graphite rods purchased from Alfa Aesar with Ni or Cu wires obtained from Nilaco corporation were used for producing CNHs via the GI-AIW method. In short, a graphite rod (diameter of 20 mm and length of 55 mm) with a centered hole (diameter of 12 mm and depth of 25 mm) was used as a cathode and the other graphite rod (diameter of 6 mm) was used as an anode. Both electrodes were submerged in de-ionized water which was employed as stable heat sink. On the top of the cathode, four narrow channels were drilled for introducing N2 at a flow rate of 10 L/min. Electrical current and voltage were supplied to the electrode rods using an arc machine equipped with a current controlling system. In addition, for maintaining the stable arc discharge, a distance between the tip of the anode and the inner surface within the hole of the cathode was steadily controlled. The anode was moved toward the static cathode at a rate of 5.25 mm/s using a motor-driven slider while a constant current of 80 A was supplied. In each arc discharge operation, 30 mm of the graphite anode was consumed and resulted in emerging of black particulate products floating on the top surface of water. Under microscopic observation, those particulate products mainly contained CNHs. After collected and dried at 90°C overnight, the resultant CNHs were further characterized using spectroscopic and gravimetric analyzers.

Similarly, CNHs hybridized with Ni nanoparticles (Ni/CNHs), CNHs hybridized with Cu nanoparticles (Cu/CNHs), and CNHs hybridized with Ni and Cu nanoparticles (NiCu/CNHs) could also be produced by the same process. Instead of pure graphitic rod, the anode was drilled axially to make a hole (diameter of 1.5 mm and length of 70 mm) for inserting metal wires (diameter of 0.03 mm, and length of 70 mm). A set of 10 Ni wires or 10 Cu wires was inserted into the anode hole for supplying metal species in the syntheses of Ni/CNHs or Cu/CNHs, respectively. For NiCu/CNHs, a set of 5 Ni wires and 5 Cu wires was used instead. Similarly, to maintain stable arc discharge operation, the moving speed of the anode was kept the same as when CNHs were synthesized.

Microscopic structures of pristine and hybridized CNHs were investigated using a transmission electron microscope (TEM) (JEOL, JEM1010), and a X-ray diffractometer (XRD) (Rigaku, UltimaIV) with CuKα radiation operated at 40 kV and 20 mA with a scanning step of 0.02° min⁻¹ in a range of 10° to 90°. An energy dispersive X-ray spectrometer (EDX) (Technix Lab, Tiny SEM/EDX) and a thermogravimetric analyzer (TGA) (Shimadzu, TGA-50) were also employed for analyses of their chemical composition and thermal stability, respectively. For detecting residual content in each sample the TGA analyses were conducted under a controlled condition of air flow within a temperature range of 30 to 900°C with a ramp rate of 10°Cmin⁻¹. Specific surface area of all hybridized CNHs was measured by N2 sorption using BET analyzer (Bel Japan, Belsorp-mini).

Conversion of D-xylose to other high value-added products, especially furfural was performed using an autoclave reactor with the presence of pristine or hybridized CNH samples. Composition of typical products was identified and analyzed for evaluating the catalytic performance of all synthesized CNHs. In short, 0.05 g of synthesized CNHs and 30 mL of 0.2 mol·dm⁻³ D-xylose solution was loaded into the 80 mL autoclave equipped with teflon liner. Magnetic bar was employed for stirring the suspension with a constant speed of 700 rpm to avoid mass transfer resistance within the autoclave reactor. In prior to being heated to 170°C, N2 was purged to remove O2.
dissolving in the liquid suspension and to increase the vessel pressure to 1.5 MPa. Resultant product was collected after being held for 4 h. 0.22 μm nylon syringe filter was used for collecting liquid sample which was analyzed by high-performance liquid chromatography (HPLC) (Shimadzu) with HPX-87H column (BIO-RAD, Aminex) in which 20 vol% of acetonitrile in 5 mmol・dm$^{-3}$ of sulfuric acid aqueous solution was used as a mobile phase with a constant flow rate of 0.6 mL・min$^{-1}$.

3. Results and Discussion

Microscopic analyses could confirm that CNHs and CNHs hybridized with metal alloy could be produced by GI-AIW method. Typical TEM images in Fig. 1 depict morphology of CNHs, Ni/CNHs, Cu/CNHs and NiCu/CNHs. Fig. 1 a) reveals CNHs as an aggregation of horn-like carbonaceous nanostructure without any other impurity. Meanwhile dark and dense spots in Fig. 1 b), c), and d) respectively reveal dispersion of Ni, Cu and NiCu nanoparticles within aggregating CNHs, which could be considered as CNHs hybridized with such metal or alloy nanoparticles. In addition, it could be clearly observed that nominal size of the metal nanoparticles were significantly dependent upon their synthesizing condition 19).

In this work, XRD analyses were performed to identify the crystallographic structure of each synthesized sample. As shown in Fig. 2, detection of diffraction peaks at 43.3° and 50.4° indicates the presence of Cu(111) and Cu(200), respectively. In addition, two distinctive peaks detected at 44.4° and at 51.7° represent Ni(111) and Ni(200), respectively. For NiCu/CNHs, the XRD peaks which appear between the locations of the characteristic peaks of pure Cu and Ni could confirm the formation of alloy in the hybridized CNH sample 20) – 22).

The thermal stability of all synthesized samples was evaluated based on TGA, which could provide information of microscopic structure and composition of the samples. As depicted in Fig. 3, the thermogram of CNHs exhibits the highest thermal tolerance when compared to those of other metal/CNH samples. Typical thermal gravimetric signal with a drastic weight reduction at 530 °C suggested the beginning of CNHs decomposition. Meanwhile, decomposition of Cu/CNHs and Ni/CNHs was detected at 350 and 450 °C, respectively. Interestingly, the decomposition of NiCu/CNHs was also detected at about 350 °C. These distinctive analyses suggest that inclusion of metal and alloy within the aggregating structure of CNHs would significantly affect their thermal stability.

![Fig. 1 TEM image of a) CNHs, b) Ni/CNHs, c) Cu/CNHs, and d) NiCu/CNHs](image-url)

![Fig. 2 XRD pattern of the catalysts](image-url)
and NiCu/CNHs exhibited a similar thermogram but a higher content of residue in NiCu/CNHs was detected. On the other hand, negligible content of remaining residue was detected in CNHs because they contained only carbon constituent.

It is notable that the higher content of residue in Ni/CNHs when compared to that of Cu/CNHs would be attributed to a difference in the condensation rate of Ni and Cu in the arc discharge reaction field. Extremely high heat flux generated by the arc discharge could vaporize Ni and Cu wires, resulting in formation of atomic Ni or Cu which would be condensed and solidified to become nanoparticles. Because the boiling point of Cu (2,562 °C) is lower than that of Ni (2,913 °C), the condensation of atomic Cu would be achieved later after the temperature became lower than its boiling point. As a result, the less amount of the Cu would be formed and engaged in the formation of hybridized CNHs.

Furthermore, compositions by weight of each synthesized sample were identified by EDX while specific surface area was measured by N2 sorption with respect to BET equation. Typical EDX and BET analytical results of all synthesized samples were summarized in Table 1. EDX analyses could confirm that there was Ni content in Ni/CNHs higher than Cu content in Cu/CNHs, resulted from the differences in condensation temperature of Ni and Cu 23. It should also be noted that CNHs possessed largest specific surface area when compared to Ni/CNHs, Cu/CNHs, and NiCu/CNHs. Nevertheless, specific surface area of either CNHs or hybridized CNHs were significantly higher than those of Al2O3 or SiO2 which were employed as catalyst support reported in other previous works 24-25. Higher specific surface area together with inclusion of metal or alloy within the hybridized CNHs which is more sensitive to thermal stimulation could suggest that such CNHs hybridized with metal (Ni, Cu) or NiCu alloy would act as catalyst which is beneficial to enhancing oxidative reactions of hydrocarbons 26.

For confirmation, the experiments on dehydration of D-xylose to furfural were also performed to evaluate the catalytic performance of CNHs and metal/CNHs. Samples of liquid product taken from repeated experiments were subject to HPLC analyzes for determining conversion of D-xylose and yield of furfural which were determined using equations (1) and (2), respectively.

Conversion of D-xylose (%)
\[
\text{Conversion} = \frac{\text{Mole of D-xylose converted (mol)}}{\text{Mole of D-xylose before reaction (mol)}} \times 100
\]

Yield of Furfural (%)
\[
\text{Yield} = \frac{\text{Mole of furfural produced (mol)}}{\text{Mole of D-xylose before reaction (mol)}} \times 100
\]

In general, dehydration of D-xylose is an autocatalytic reaction which could result in formation of furfural and other derivatives. Under a high temperature condition, water could behave as an active medium for the dehydration of D-xylose, resulting in formation of furfural because it could provide H+ and OH- ions which would efficiently act as acid- and based-catalysts 27-28. There are some previous works suggesting possible reaction pathways of furfural formation together with some side reactions, i.e. isomerization, fragmentation, condensation, and resinification. As a result, formation of some organic acids and solid product (humin) which are undesirable by-products would take place1-14. As shown in Fig. 4, with the absence of any catalysts, the conversion of D-xylose and yield of furfural were approximately 43.1% and 27.9%, respectively. With the presence of CNHs, slightly enhanced catalytic activity was confirmed in term of D-xylose conversion and furfural yield. Interestingly, with the presence of Ni/CNHs both D-xylose conversion and furfural yield could be most enhanced. However, Cu/CNHs exerted the lowest catalytic activity while NiCu/CNHs provided relatively low catalytic activity when compared to that of Ni/CNHs. Taking into account all experimental results suggested that the hybridization of Ni, Cu, and Ni/Cu with CNHs would attribute to D-xylose conversion and also further conversion of furfural to other by-products due to

| Catalysts | Compositions by EDX (wt.%) | Specific surface area (m²·g⁻¹) |
|-----------|---------------------------|-------------------------------|
| CNHs      | 100 - -                    | 169                           |
| Ni/CNHs   | 79.4 20.6 -                | 161                           |
| Cu/CNHs   | 86.6 - 13.4                | 145                           |
| NiCu/CNHs | 79.7 7.7 12.6              | 143                           |
other side reactions.

It should be noted that Ni, Cu, and NiCu could act as Lewis acid sites. Weingarten et al. (2011) reported some solid catalysts with a certain number of Lewis acid sites could predominantly enhance conversion of D-xylose through the dehydration process. In general, Cu which is recognized as a strong Lewis acid site could promote other side reactions to convert either D-xylose or furfural to humin. Therefore, with the presence of Cu/CNHs, selectivity of furfural would inevitably be affected, resulting in relatively low yield of furfural though a high conversion of D-xylose could be achieved. Meanwhile, Ni would play a role in selectively convert D-xylose to furfural with less side reaction. Some other previous works also experimentally confirmed that Ni could enhance the performance of Cu catalyst under the reactive environment of high pressure. It is suggested that a possible strategy to increase the selectivity of furfural would be achieved by introducing Brønsted acid sites. Therefore, control of appropriate ratio of Brønsted to Lewis acid sites available on such NiCu/CNH catalyst would be an issue for further exploration in the future. The optimization of Ni to Cu ratio should be a potential approach to enhance the furfural yield from dehydration of D-xylose or other derivatives.

4. Conclusion

Synthesis of CNHs hybridized with Ni, Cu or NiCu could be achieved and controlled by one-step GI-AIW method. Content of Ni or Cu nanoparticles in the Ni/CNHs or Cu/CNHs was regulated by difference in condensation temperature of Ni or Cu, respectively. Ni/CNHs exhibited the highest conversion of D-xylose and the highest yield of furfural. Further investigation on effect of Ni to Cu ratio together with optimized reaction condition would be a key issue to improve productivity of furfural from dehydration of D-xylose and derivatives.

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