LIQUEFACTION OF CORN DISTILLERS DRIED GRAINS WITH SOLUBLES (DDGS) IN HOT-COMPRESSED PHENOL

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The present work aims to liquefy corn Distillers Dried Grains with Solubles (DDGS), a by-product in corn ethanol production, to produce liquid products as a potential substitute for petroleum-derived phenol or an additive in the manufacturing of phenolic resins. Efficient liquefaction of DDGS has been realized with hot-compressed phenol at 200-450°C. Effects of liquefaction temperature, initial phenol/DDGS ratio (wt/wt), residence time, and catalysts on yields of liquefaction products, as well as characterizations of typical liquid and solid products, have been investigated. The yield of liquid products increased with temperature, while it peaked at around 300°C, due to condensation/cracking reactions of the liquid intermediates/products to form solid products (i.e., coke/char) at temperatures higher than 300°C. The liquid yield increased monotonically with the initial phenol/DDGS ratio for a specified treatment time and temperature. An increased residence time generally produced a lower yield of liquid products, and a higher yield of solid residue, which was likely due to the increased coke/char formation from liquid products for a prolonged residence time. The yield of liquid products reached a maximum of 97 wt% at 300°C for 5 min-operation with Phenol/DDGS of 2/1. K_2CO_3, Rb_2CO_3, and NaOH were found very effective catalysts for enhancing the liquid yields. The use of these catalysts resulted in a 25% relative increase in the liquid yields for 5 minute operation with Phenol/DDGS of 1/1 at 300°C.

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INTRODUCTION

Ethanol as a renewable transportation fuel has been widely used to partially replace gasoline (up to 10%) in the US and Canada. Blending ethanol with gasoline can significantly reduce greenhouse gases emissions. In addition, ethanol can be an environmentally friendly alternative to methyl tertiary butyl ether (MTBE), a typical gasoline additive for cleaner combustion (McCarthy and Tiemann 1998). Driven by the declining oil reserves, skyrocketing oil prices, and the increasing concerns over greenhouse gases emissions, there has been a dramatically increased demand for fuel ethanol in recent years. For instance, the US produced 12.9 billion litres of fuel ethanol in 2004, almost double its production in 2001 (i.e., 6.7 billion litres) (Fulton 2004). Canada produced 250 million litres of fuel ethanol in 2004, compared with about 175 million

litres in 2002. Although significant research efforts in recent years have been made on technologies for producing cellulosic ethanol from the abundant resources of lignocellulosic materials (Cuzens and Miller 1997; Sun and Cheng 2002, 2005), fuel ethanol is mainly produced from corn grains in North America. When ethanol is produced from corn, only the starch is used, while the remaining protein, fiber, vitamins, and minerals in dry mill corn processing are recovered as by-products such as Distillers Dried Grains (DDG) and Distillers Dried Grains with Solubles (DDGS). One bushel of corn produces 18 pounds (2.72 gallons) of ethanol and approximately 17 pounds of DDGS, and approximately 3.2 to 3.5 million metric tonnes of DDGS are produced annually in North America.

In recent years the demand for fuel ethanol has sent corn prices soaring, close to $4 per bushel, about double the price of two years ago. Marketing the by-product DDGS is thus becoming important to the sustainability of fuel ethanol plants. DDGS are primarily utilized as animal feed (Perry 1984; Silke and Udén 2006). Recently, interest has been growing in alternative uses of DDGS. For instance, Wang et al. (2007) have successfully separated lipid compounds from DDGS using supercritical CO_2 extraction, which could be further refined to concentrate fatty acids, policosanols, phytosterols, and tocols. Recovery of the fibre components in DDGS was also realizable by filtration and centrifugation (Udén 2006). Another potential use of DDGS may be production of liquid chemicals by employing thermo-chemical liquefaction technologies such as fast pyrolysis and high-pressure direct liquefaction. To the best of the authors' knowledge, however, no work has been reported so far on liquefaction of DDGS.

In contrast, there was an immense interest in liquefying biomass for renewable liquid fuels and chemicals through fast pyrolsyis (Maschio et al. 1992; Onay and Kockar 2006) or high-pressure direct liquefaction (Appell 1967; Yokoyama et al. 1984; Minowa et al. 1998). Compared with the fast pyrolysis technology (normally operating at a high temperature of 400-1000°C and producing water-rich and highly acidic bio-oils at a yield of 50-70 wt%), high-pressure direct liquefaction processes (operating at a mild temperature between 200 and 400°C) are advantageous in view of energy consumption. High-pressure direct liquefaction of biomass is normally operated in a hot or hot-compressed solvent such as water or organic solvents including alcohols (Miller et al. 1999; Xu and Etcheverry 2007), ethylene glycol (Rezzoug and Capart 2003), cyclic carbonates (Yamada and Ono 1999) and phenol (Maldas and Shiraishi 1997). Among all the biomass-derived chemicals being exploited, phenols and derivatives have received greater interest, because of the soaring prices of benzene and phenol in recently years and the rapidly-increased demand in phenolic resins for the engineered wood products (plywood, oriented strand board and particleboard panels). The high oil prices have also led to increased costs for synthetic resins at a time when the demand for engineered wood products is also climbing. Therefore, there is a strong need of producing phenol substitutes from natural resources such as forest/agricultural biomass/wastes. In a biomass direct liquefaction process, phenol and phenolic compounds may be formed directly from lignin by de-polymerization and indirectly from the cellulose/hemi-cellulose-derived carbohydrates in the presence of a suitable catalyst (Sinag et al. 2004).

During the past several years, significant efforts have been made on completely or partially replacing petroleum-derived phenol with lignocellulosic waste materials. Many

studies have been conducted to find economically and environmentally friendly substitutive starting materials for phenol in the manufacturing of phenol-formaldehyde resins. Lignin is a highly cross-linked, three-dimensional aromatic polymer with phenylpropane units linked together by carbon-carbon or ether bonds and with phenolic and alcoholic hydroxyl groups, thus lignin has tremendous potential for many industrial uses as substitutes for the depleting and expensive petroleum-based materials such as phenols. Various types of lignin, including kraft, black liquor, lignosulfonate, soda-anthraquinone and organosolv have been tested as phenol substitutes for the synthesis of lignin-modified phenol-formaldehyde resins (Benar et al. 1999; Danielson and Simonson 1998; Turunen et al. 2003). Limitation has been however found for the direct use of lignin as the substitutive phenol in the manufacturing of phenol-formaldehyde resins because of the low reactivity of lignin due to its complex chemical and physical structures. It has been demonstrated that chemical modification such as phenolation of lignin (treated with phenol at a low temperature, e.g., 70°C) is an effective approach to improve the lignin reactivity (Cetin and Ozmen 2002).

Compared with the direct substitution of lignin or lignocellulosic wastes for phenol in the synthesis of phenolic resins, liquefying lignocellulosic materials first into liquid products that are subsequently used as the phenolic feedstock for the resin synthesis proved to be more promising, since it has the potential for total replacement of petroleum-derived phenol with renewable resources. Hot or hot-compressed phenol was found very effective for liquefying lignocellulosic materials such as wood (Alma et al. 2001; Lee and Ohkita 2003), grapevine cane (Alma and Basturk 2006), corn bran (Lee 2003) and Tannin (Santana et al. 1995). Another advantage of using phenol as the liquefaction solvent is that the un-reacted phenol together with the reacted phenol as well as the liquefied biomass may be directly used as the feedstock for the synthesis of phenolic resins.

In addition to lignin or lignocellulosic materials, corn or wheat starch (a natural polysaccharide) has also been used as a modifier or additive in the manufacturing of phenolic resins for dry-out resistance and improved prepress tack (Sellers 1985). It was also found that starch could be an effective additive to phenolic resins for improved condensation viscosity (Turunen et al. 2003). To explore alternative uses of DDGS, the by-product in the production of corn ethanol, it is of interest to examine the potential of employing DDGS (containing mainly proteins, fat, fibre and nitrogen-free extracts) as an additive in the synthesis of phenolic resins.

The objective of this work was thus to liquefy corn DDGS in hot-compressed phenol to produce liquid products as a potential phenol substitute or an additive for the synthesis of phenolic resins. Effects of the liquefaction conditions including temperature, residence time, solvent-to-DDGS ratio, and catalysts on the liquefaction yields were examined. The liquefaction products were separated into fractions of gas, methanol soluble, and solid residue (methanol insoluble products, which were further characterized by gas chromatograph (GC), gas chromatograph equipped with a mass selective detector (GC/MS) and x-ray diffraction (XRD), respectively.

EXPERIMENTAL

Materials

The sample of corn DDGS used in this study was donated from GreenField Ethanol, Canada's leading fuel and packaged alcohol producer. The original sample was milled into fine powder smaller than 20 mesh (~ 0.8 mm). The powder was dried in an oven at 105°C for 24 hours before use. The proximate and ultimate analysis results of the DDGS sample and the compositions of major inorganic elements in the sample are given in Table 1. The dried DDGS sample contained 3.8 wt% ash, and a high concentration of nitrogen at 4.1 wt% due to its high content of protein. The major metal/non-metal elements in the DDGS sample identified by ICP-AES were Mg, K, Na, S and P. The solvents used, i.e., phenol (in crystal form) and methanol, and the catalyst compounds tested, including NaOH (50 wt%), K_2CO_3 and Rb_2CO_3, were all A.C.S. reagents.

Table 1. Proximate and Ultimate Analyses of the DDGS Sample and Concentrations of Major Metal/Non-metal Elements

Proximate analysis, wt% (d.b.[1])		Ultimate analysis, wt% (d.a.f.[2])				
Organics	Ash	C	H	N	S	O[3]
96.2	3.8	49.8	6.7	4.3	0.7	38.5

Major metal/non-metal elements, ppmw (d.b.)[4]									
Na	K	Mg	Ca	Fe	Zn	Al	Si	P	S
751	9287	3074	177	99	53	20	53	8137	6504

[1] On a dry basis; [2] On a dry and ash-free basis; [3] By difference; [4] by ICP-AES.

Liquefaction Experiments

The experiments were carried out with a micro-reactor system whose schematic diagram is given elsewhere (Xu and Etcheverry 2008; Xu and Lancaster 2008). The micro-reactor with an effective volume of 14 ml was made of stainless steel (SS 316L), and it consisted of capped 5/8 inch Swagelok bulkhead unions. In a typical run, 1.0-3.0 g of the DDGS sample was weighed into the reactor, followed by adding 5.0-3.0 g of pure phenol crystal, corresponding to a phenol-to-DDGS ratio or phenol/DDGS (wt/wt) of 5/1~1/1. In the liquefaction runs where a catalyst was used, the amount of the catalyst added was fixed at 5.0 wt% of the mass of dry DDGS in the reactor. The reactor was securely sealed, and the air inside the reactor was displaced with ultrahigh purity nitrogen by repetitive operation of vacuuming and N_2-charging. Finally, the reactor was pressurized with 2.0 MPa N_2 to prevent boiling of the solvent during the liquefaction operations. Supported on a mechanical shaker (set at 100 rpm), the reactor was then rapidly immersed in a fluidized sand bath that was preheated to a specified temperature. After the desired reaction time has elapsed, the reactor was removed from the sand bath and quenched in a water bath to stop the reactions. All the experimental runs were

repeated two or three times, and the maximum error in the product yields between the runs under the same conditions was ensured within 3%.

Separation of Liquefaction Products

Once the reactor was cooled to room temperature, the gas inside it was vented into a Teflon gas-bag. The collected gas products (designated simply as "Gas") were analyzed with gas chromatograph, using a thermal conductivity detector (GC-TCD). The solid/liquid products were rinsed completely from the reactor with methanol. The resulting suspension was filtered under reduced pressure through a pre-weighed Whatman No. 5 filter paper to recover the solid residue which was methanol-insoluble (simply denoted as "Solid" hereinafter), consisting of un-reacted DDGS sample, coke/char and ash (assuming the catalyst compounds were soluble in the liquid products). The solids that were retained by the filter paper were dried for 2 hours in the oven at 105°C before weighing. The filtrate was evaporated under vacuum at 40°C to remove the methanol solvent, and the resulting liquid (i.e., methanol soluble) contained liquid products derived from the added DDGS (denoted simply as "Liquid" hereinafter), and reacted/un-reacted phenol solvent, and maybe some residual methanol that was combined to the liquid products. It should be noted that in the above evaporation operation for separating methanol from the liquid products, the "light ends" products could be lost due to their low boiling points, and the interaction between methanol and the liquid products would cause a difficulty for complete removal of methanol from the liquid products. In the present work, the yields of Gas, Solid, and Liquid were all calculated to the dry organic matters of the added DDGS (i.e., on a dry and ash-free basis). It was reasonably assumed that the recovered solid residues contained all the ash that was present in the DDGS sample added. As such, in the calculation of the Solid yield, the mass of solid residue was corrected on the dry and ash-free basis by excluding the ash amount from the dry mass of the solid residue. It was further assumed that the total mass of the phenol solvent remained approximately unchanged during the liquefaction operations, while the added phenol solvent could be present in the forms of both reacted and un-reacted phenol in the resulting liquid. With this assumption, the yield of Liquid (i.e., the liquid products derived directly from DDGS) could be simply obtained by difference, i.e., *(Liquid Yield) = 100 wt% - (Solid Yield) – (Gas Yield)*.

Product Characterizations

The liquid products were analyzed with a gas chromatograph equipped with a mass selective detector [Varian 1200 Quadrupole GC/MS (EI), Varian CP-3800 GC equipped with VF-5 ms column (5% phenyl 95% dimethylpolysiloxane, 30 m×0.25 mm×0.25 μm); temperature program: 40°C (hold 2 min) →190°C (12°C/min) → 290°C (8 °C/min, hold 20 min)]. X-ray diffraction (XRD) measurements for the crude DDGS powder and the solid residues recovered from the liquefaction experiments were carried out using Ni-filtered Cu-Kα radiation with a Philips PW 1050-3710 Diffractometer, in order to examine the evolution of the crystalline forms in the DDGS samples during the liquefaction operations.

RESULTS AND DISCUSSION

Effects of liquefaction temperature, phenol/DDGS ratio, residence time, and catalysts on the yields of liquefaction products, as well as the characterizations of typical liquid and solid products are discussed below. The major gaseous species in the Gas products identified by GC-TCD were CO_2, CO, and CH_4, while as expected the total Gas yields were very low (<5 wt%) in all the operations, as shown in Figs. 1 through 3.

Effect of Temperature

The effects of temperature on the yields of liquefaction products can be discerned from Fig. 1, which presents results obtained from the liquefaction operations at various temperatures ranging from 200°C (with hot-compressed phenol) to 450°C (with supercritical phenol) for a same residence time of 30 min without catalyst, where the Phenol/DDGS ratio was fixed at 5/1.
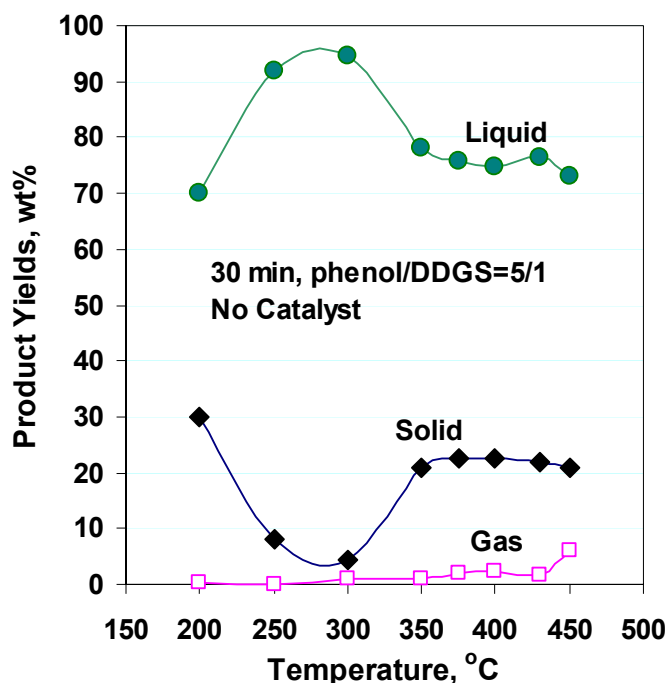

Fig. 1. Variation in the product yields with reaction temperature

The results in the figure reveal that hot-compressed phenol was a very effective solvent for liquefaction of DDGS, producing liquid products at a yield of >70 wt% at > 200°C, as similarly observed in many studies on liquefaction of lignocellulosic materials using phenol (Alma et al. 2001; Lee and Ohkita 2003; Lee 2003). As also shown in the figure, the Liquid yield increased dramatically at the expense of the Solid yield as the liquefaction temperature increased up to 300°C. The Liquid yield attained a maximum of about 95 wt% at 300°C. As the reaction temperature further increased from 300°C to 450°C, the Liquid yield reduced, which was accompanied by an increase in the Solid

formation. The reverse trends between the yields of liquid products and solid residue versus temperature above 300°C may suggest conversion of liquid products to solid residue during the treatment. The conversion of liquid products to solid residue as observed here at a high temperature (>300°C) was likely due to condensation/cracking reactions of the liquid intermediates/products forming solid (e.g., coke/char) and gas products in the process, as similarly observed by Qu et al. (2003) and Holliday et al. (1997). The formation of coke/char at >300°C was evidenced by the XRD results (presented later in Figure 7). The occurrence of the condensation/cracking reactions of the liquid products may also be evidenced by the apparently increased yields of Solid and Gas from 350°C to 450°C, as shown in Fig. 1.

It has been well documented in many previous studies that temperature is the most critical parameter for the liquefaction of lignocellulosic materials (such as wood) in water or an organic solvent. For example, when biomass was heated in hot compressed water, solvolysis of hemicellulose and lignin began to occur at > 190°C, and all of the hemicellulose and much of the lignin dissolved in the water at 220°C (Mok and Antal 1992; Allen et al. 1996), forming the intermediates or products of liquid products. Solvolysis and pyrolysis of the remaining lignocellulosic solids took place at a higher temperature, producing intermediates that could undergo an extraordinary variety of reactions such as isomerization, dehydration, fragmentation and condensation reactions, and ultimately form liquid oils, gas and char (Antal et al. 1990; Bobleter 1994). When liquefied in phenol with the presence of HCl as a catalyst, wood could be phenolated at a conversion of 25 wt% in the treatment at a temperature as low as 60°C for 30 min (Acemioglu and Alma 2002).

Effect of Initial Phenol/DDGS Ratio

The effect of initial phenol/DDGS ratio was investigated by conducting the liquefaction operations with a phenol-to-DDGS ratio varying from 1.0 to 5.0, for a residence time of 30 min at 300°C without catalyst. The results are illustrated in Fig. 2. It is not surprising that a higher initial phenol/DDGS ratio produced a larger conversion of the solid and a greater yield of liquid products. The Liquid yield was less than 80 wt% in the operation with a phenol/DDGS ratio of 1/1, compared with 95 wt% at a phenol/DDGS ratio of 5/1. It is likely that a lower phenol concentration may restrict solvolysis of the DDGS solids and promote condensation reactions of the DDGS-degraded intermediates and liquid products, leading to a smaller yield of liquid products and a higher yield of solid residue as evidenced in Fig. 2. The initial phenol/DDGS ratio showed negligible influence on the Gas yields (all < 5 wt% under the present experimental conditions).
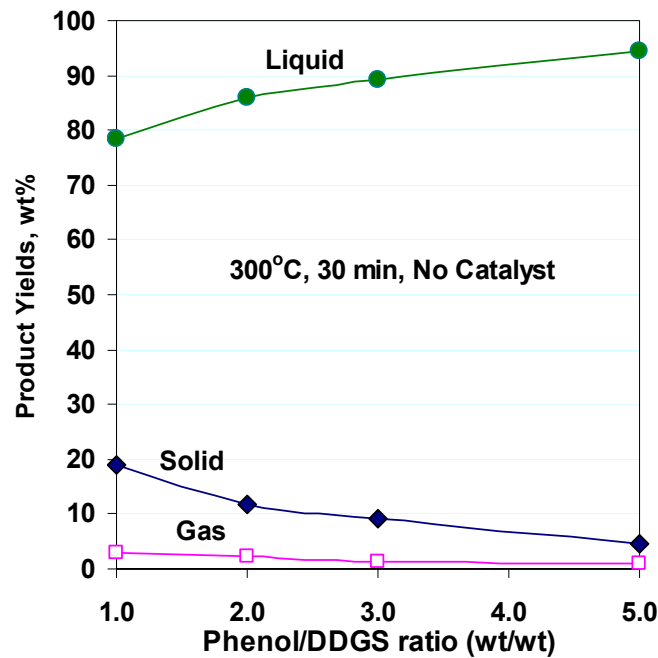
Fig. 2. Variation in the product yields with initial phenol/DDGS ratio

Effect of Residence Time

Fig. 3 shows the yields of liquefaction products from DDGS (with the Phenol/DDGS ratio fixed at 2/1) at 300°C for various lengths of time (2-60 min), all without catalyst.
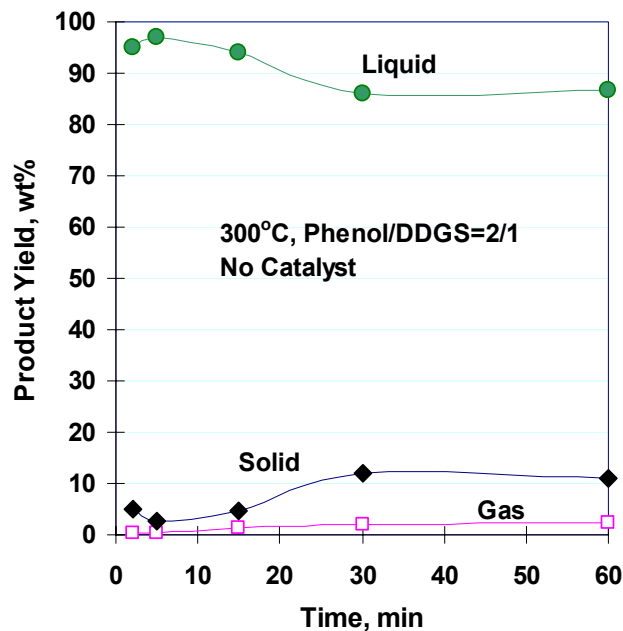

Fig. 3. Variation in the product yields with residence time

An interesting observation was that the DDGS conversion (revealed from the Solid yields in the figure) as well as the Liquid yield appeared to reach a maximum at 5 min. The yield of liquid products attained as high as 97 wt% at 5 min, compared with about 95 wt% at 2 min and 86 wt% at 30 min. From Fig. 3, an increased residence time generally produced a lower yield of liquid products but a higher yield of solid residue, which was very likely due to condensation/cracking of the liquid products/intermediates for a prolonged residence time, resulting in a build-up of coke/char, as discussed earlier in Fig. 1. This result may suggest that the optimum treatment time for DDGS in phenol would be around 5 min and a longer treatment time would reduce the yields of liquid products due to the enhanced condensation/cracking reactions of the liquid products/intermediates. As shown in Fig. 3, the Gas yield monotonously increased as the residence time increased.

Effect of Catalysts

Figures 4 and 5 show the effects of various catalysts (NaOH, Rb_2CO_3, and K_2CO_3) on liquefaction of the DDGS in phenol (with the Phenol/DDGS ratio fixed at 1/1) for 5 min at temperatures ranging from 200°C to 350°C.
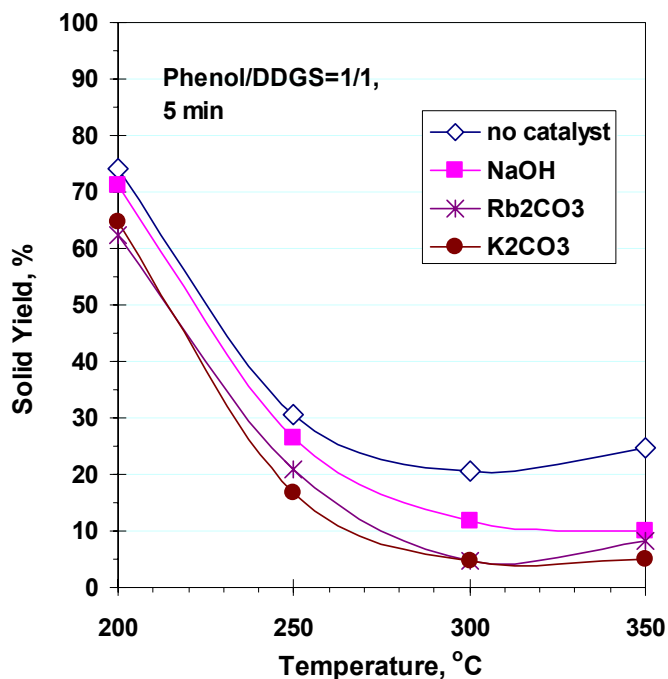

Fig. 4. Effects of catalysts on yield of solid residue

Alkali compounds, e.g., Na_2CO_3, NaOH, K_2CO_3, KOH, LiOH, RbOH, and CsOH, etc., have been widely employed as catalysts in direct-liquefaction of agricultural/forest biomass to suppress the formation of char and to enhance the yield of liquid products (Minowa et al., 1998; Karagoz et al., 2005). Alkalis (e.g., NaOH and $Ca(OH)_2$) and acids (e.g., H_2SO_4 and HCl) were also proved to be effective for phenolysis of biomass in

phenol (Maldas and Shiraishi 1997; Alma et al. 1996 and 1998; Alma and Basturk 2006). The performance of the selected catalysts in liquefaction of the DDGS with phenol can be revealed from Figs. 4 and 5 (for the yields of solid residue and liquid products, respectively). At all temperatures tested, as expected, the presence of a catalyst in the liquefaction system dramatically enhanced solid conversion, accompanied by a significantly increased Liquid yield. The catalytic effects for all the catalysts were more evident at a higher temperature while their activities appeared to level off at 300°C. At all temperatures tested, the catalysts for enhancing solid conversion and Liquid yield exhibited an activity sequence of $Rb_2CO_3 \approx K_2CO_3 > NaOH$. The presence of 5 wt% K_2CO_3 or Rb_2CO_3 produced a Liquid yield of about 95 wt% in relation to only 75 wt% without catalyst at 300°C. Or in other words, the use of these catalysts resulted in 25% relative increase in the liquid yields for 5 min-operation with Phenol/DDGS of 1/1 at 300°C.
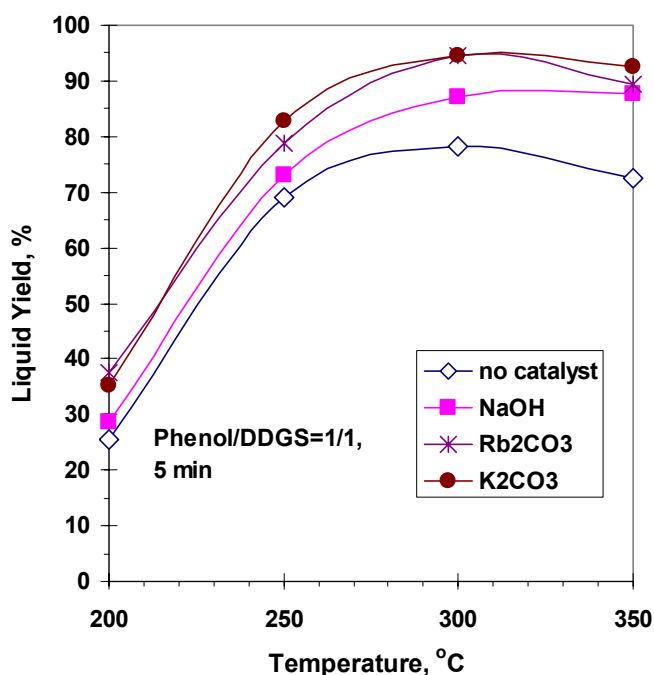

Fig. 5. Effects of catalysts on yield of liquid products

As mentioned earlier, alkaline solutions of Na_2CO_3, NaOH, K_2CO_3, KOH, LiOH, RbOH, and CsOH, etc., were proven to be effective for suppressing the char formation and enhancing Liquid yields in biomass liquefaction (Minowa et al. 1998; Karagoz et al. 2005). The following catalytic mechanism of the alkaline solution as the catalyst for the carbohydrate liquefaction process in the presence of carbon monoxide was proposed by Appell et al. (1967). Taking Na_2CO_3 (or CO_3^{2-}) and NaOH (or OH^-) as the examples:

1) Reaction of carbonate/hydroxide ions with carbon monoxide to form formate and carbon dioxide.
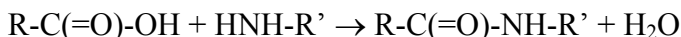
$$CO_3^{2-} + 2CO + H_2O \rightarrow 2HCOO^- + CO_2 \text{ or } OH^- + CO \rightarrow HCOO^-$$

2) Dehydration of vinical hydroxide groups in the carbohydrate biomass feed to an enol and the further isomerization to ketone.

$$-CH(OH)-CH(OH)- \rightarrow -CH=C(OH)- \rightarrow -CH_2-CO-$$

3) Reduction of newly formed carbonyl group to the corresponding alcohol with formate ion and water.

$$HCOO^- + -CH_2-CO- \rightarrow -CH_2-CH(O^-)- + CO_2$$
$$-CH_2-CH(O^-)- + H_2O \rightarrow -CH_2-CH(OH)- + OH^-$$

4) Regeneration of formate ion from hydroxyl ion and carbon monoxide

$$OH^- + CO \rightarrow HCOO^-$$

The resulting intermediate compounds such as ketone, carbonyl, and alcohol groups will then re-arrange to form liquid products through a series of reactions such as dehydration, dehydrogenation, deoxygenation, decarboxylation, and condensation. The above mechanism was proposed for the reaction system in the presence of CO, which is different from that for the present study where N_2 instead of CO was used. However, CO was one of the major gaseous species (along with CO_2 and CH_4) formed in the treatment, as evidenced by our GC-TCD analysis for the Gas products, and hence the above mechanism might still play an important role in the present system. The adoption of the above mechanism could also effectively account for the observation that a higher formation of CO_2 was obtained in the presence of a catalyst.

Characterizations of the Liquid and Solid Products

The liquid products were analyzed with a gas chromatograph equipped with a mass selective detector, and the chemical compounds in the Liquid were identified in terms of the NIST 98 MS library with the 2002 update. Figure 6 presents a portion of the GC/MS chromatograph for the liquid product from the liquefaction operation (phenol/DDGS = 5/1) at 450° for 30 minutes without catalyst. As expected, the chromatograph contains a dominant peak (assigned to the un-reacted phenol from the liquefaction solvent added) at RT = 7.242 min and many peaks registered as phenolic compounds (such as 2-methyl-Phenol, 4-methyl-Phenol, 2-ethyl-Phenol, and 3,4-dimethyl-Phenol, etc.), and phenol derivatives (such as 2-methyl-Benzofuran, Ethyl-2-benzofuran, 2,3-dihydro-3,3-dimethyl-1H-Indene-1-one, Dibenzofuran, 4-methyl-Dibenzofuran, and 9H-Xanthene). This dominant phenol peak might consist of some quantity of individual phenol formed from DDGS during the liquefaction operations, but the authors believe that the DDGS-derived individual phenol was negligible due to the composition of the DDGS feedstock. As well known, the corn DDGS feedstock typically contains only 10 wt% fibre, balanced by protein, fat, ash and nitrogen-free extracts (Belyea et al. 2004). Thus, unlike the liquefaction of a woody biomass containing a significant amount of lignin component that could be degraded into phenol by de-polymerization during liquefaction (Xu and Etcheverry 2008), liquefaction of corn DDGS would not likely generate an appreciable amount of individual phenol. No amino acid was detected by GC/MS in the liquid products from DDGS after being treated in

hot-compressed phenol. Instead, some nitrogen-containing compounds such as 5,7-dimethyl-1H-Indazole, N-(xanthen-9-yl)-p-Toluenesulfonamide and 8-Dimethylamino-naphthalene-1-carbonitrile, etc. were detected by GC/MS. It is well known that the dehydration (condensation) reaction between two amino acids, as shown below, would form a peptide bond and an amide.

$$R\text{-}C(=O)\text{-}OH + HNH\text{-}R' \rightarrow R\text{-}C(=O)\text{-}NH\text{-}R' + H_2O$$

Dehydration of amides would further produce nitrile ($R\text{-}C\equiv N$) (Kuo et al., 2007). Thus, the protein components as well as the rest of nitrogen-free components such as fat and fibre and extracts in the DDGS were likely decomposed through dehydration, pyrolysis and phenolysis during the treatment. The decomposed/degraded components might form light ends, gaseous products, and more likely combine with phenol to form some phenolic compounds as observed in Fig. 6.
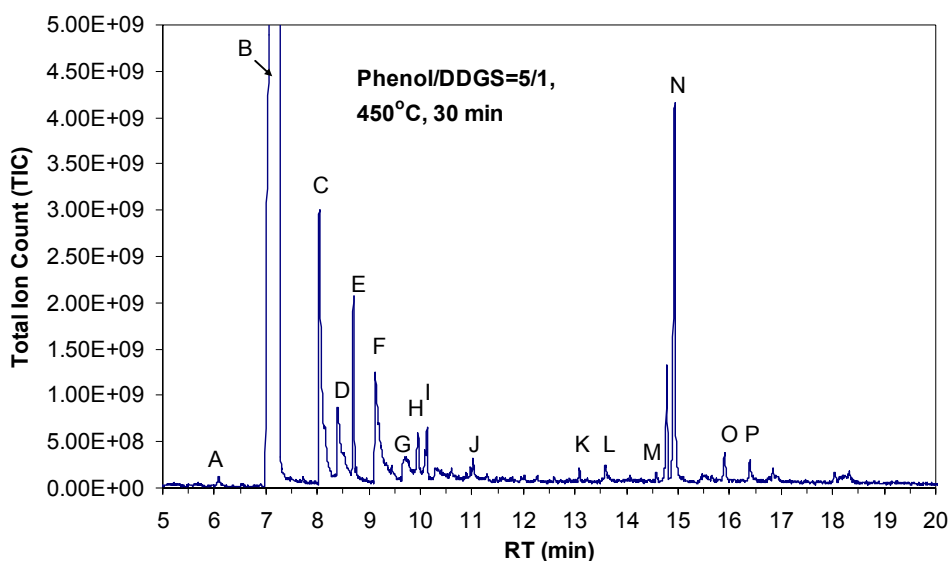

Fig. 6. GC/MS spectrum and results for the liquid product from liquefaction of DDGS in phenol (Phenol/DDGS = 5/1) at 450°C for 30 min

A = Benzene, methoxy-; B = Phenol; C = Phenol, 2-methyl-; D = Phenol, 4-methyl-; E = Benzofuran, 2-methyl-; F = Phenol, 2-ethyl; G = Phenol, 3,4-dimethyl-; H = Ethyl-2-benzofuran; I = 1H-Indazole, 5,7-dimethyl-; J = 1H-Indene-1-one, 2,3-dihydro-3,3-dimethyl-; K = Heptane, 2,2,3,3,5,6,6-heptamethyl-; L = Dibenzofuran; M = Dibenzofuran, 4-methyl-; N = 9H-Xanthene; O = p-Toluenesulfonamide, N-(xanthen-9-yl)-; P = 8-Dimethylaminonaphthalene-1-carbonitrile

The GC/MS analysis results for the liquid products from the liquefaction operations (phenol/DDGS = 5/1) for 30 min at 400 and 450°C are summarized in Table 2, while the results for the liquid products at 300°C are given separately in Table 3. The area percentage for each compound identified (defined by percentage of the compound's chromatographic area out of the total area) and the total area percentage for all the listed

compounds are shown in these tables. As expected, the un-reacted phenol was the dominating compound in each liquid product, and the relative concentration of un-reacted phenol increased from 48.5% at 300°C to 70.6% and 74.5% as the operation temperature increased to 400°C and 450°C, respectively, suggesting an increased reacted phenol at a lower operation temperature.

Table 2. GC/MS Analysis Results for the Liquid Products from DDGS after Liquefaction in Phenol (Phenol/DDGS = 5/1) for 30 min at 400°C and 450°C

RT (min)	Compound Name	Area %	
		400°C	450°C
6.052	Benzene, methoxy-	0.1	0.2
7.242	Phenol	70.6	74.5
8.02	Phenol, 2-methyl-	6.3	6.6
8.378	Phenol, 4-methyl-	2.0	2.4
8.67	Benzofuran, 2-methyl-	2.3	2.0
9.095	Phenol, 2-ethyl-	4.6	3.1
9.415	Ethanone, 1-(2-hydroxyphenyl)-	0.5	–
9.605	Phenol, 4-ethyl-	0.5	–
9.685	Phenol, 3,4-dimethyl-	0.6	0.7
9.898	1H-Indene-1,2-diol, 2,3-dihydro-1-methyl-,cis-	0.9	–
9.924	Ethyl-2-benzofuran	0.9	0.6
10.065	1H-Indazole, 5,7-dimethyl-	0.9	0.7
10.219	Phenol, 2-propyl-	0.5	–
10.419	1,3,6-Cycloheptatriene-1-acetic acid,6-hydroxy-5-oxo-	0.9	–
10.546	1,3-Cyclopentadiene, 1,2,3,4,5-pentamethyl-	0.3	–
10.572	Benzene, 1-(1-methylethenyl)-4-(1-methylethyl)-	0.1	–
10.636	Phenol, 4-(1-methylpropyl)-	0.1	–
10.874	Urea, 1-(2-methylphenyl)-3-propyl-	0.1	–
10.995	1H-Indene-1-one, 2,3-dihydro-3,3-dimethyl-	0.2	0.2
13.058	Octadecane, 3-ethyl-5-(2-ethylbutyl)-	0.3	–
13.593	Dibenzofuran	–	0.3
14.576	Dibenzofuran, 4-methyl-	–	0.1
14.901	9H-Xanthene	1.3	5.3
15.858	9H-Fluorene-3-ol, 9,9-dimethyl-	4.1	–
16.347	p-Toluenesulfonamide, N-(xanthen-9-yl)-	0.2	0.4
16.395	8-Dimethylaminonaphthalene-1-carbonitrile	–	0.4
16.792	Benzofuran, 2,3-dihydro-2-methyl-7-phenyl-	0.3	–
18.036	9H-Carbazol-3-amine, 9-ethyl-	–	0.1
18.257	Pentadecanenitrile	0.1	–
18.325	Octadecanenitrile	–	0.1
18.721	9-Octadecenoic acid, 12-(acetyloxy)-,methyl ester,[R-(Z)]-	0.3	–
24.007	Eicosanenitrile	0.1	–
25.857	Hexadecanamide	0.1	–
26.039	Benzene, (3-octylundecyl)-	0.2	–
26.131	Methanone, [1,1'-biphenyl]-4-ylphenyl-	–	0.2
30.025	Phenolsulfonphthalein	0.2	0.1

These results appeared to be contradictory to the observation of Acemioglu and Alma (2002), who observed that the amount of reacted phenol increased with temperature during phenolysis of wood at low temperatures up to 150°C. This inconsistency might be due to the wide differences between treatment conditions of the present study and those for the work of Acemioglu and Alma (2002), in raw material (DDGS vs. Birch wood), temperature (200 ~ 450°C vs. 150°C), pressure (high vs. atmospheric), and atmosphere (N_2 vs. air).

The present results may be accountable from the standpoint of thermodynamics: the phenolysis or phenolation reactions are exothermic, and they are therefore thermodynamically favorable at a lower temperature, as observed in the present study. Admittedly, unlike HPLC, GC/MS can only be a qualitative tool, and the GC-MS analysis results for liquid products have a limitation in that non-volatile compounds in the liquid products are not able to be effectively separated and detected.

Table 3. GC/MS Analysis Results for the Liquid Product from DDGS after Liquefaction in Phenol (Phenol/DDGS = 5/1) for 30 min at 300°C

RT (min)	Compound Name	Area %
7.436	Phenol	48.5
8.685	Benzene, 1-ethoxy-4-methyl-	0.7
9.373	Benzofuran, 2-methyl-	1.4
15.837	9H-Xanthene	0.8
21.243	5,10-Diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo(1,2-a;1',2'-d)pyrazine	0.9
22.443	4,4'-Ethylidenediphenol	14.6
23.232	Phenol, 2,2'-methylenebis-	2.9
25.747	Naphthalene, 6,7-diethyl-1,2,3,4-tetrahydro-1,1,4,4-tetramethyl-	1.8
25.895	1,8-Diethyl-3,6-diazahomoadamantan-9-ol	1.0
26.111	s-Indacene, 1,2,3,5,6,7-hexahydro-1,1,4,8-tetramethyl-	1.2
26.483	Oleic Acid	1.0
26.58	Z,Z-3,15-Octadecadien-1-ol acetate	1.0
27.072	1,1,2,2-Tetrakis(4-hydroxyphenyl)ethane	2.9
27.213	9-Octadecenamide, (Z)-	0.9
27.791	Benzo[e](1H)indene, 1,2,3a,4,5,9b-hexahydro-7-methoxy-3-oxo-3a,9b-dimethyl-	1.1
28.903	1,3-Phenylene, bis(3-phenylpropenoate)	0.8
29.396	3-Hydroxy-D-homoestra-1,3,5(10),8,14-pentaen-17a-one	1.6
31.146	Phenolsulfonphthalein	4.7
31.727	Phenyl palmitate	1.7
33.706	9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl)ethyl ester	4.9
33.967	Cholestan-3-one, cyclic 1,2-ethanediyl acetal,(5.alpha,)-	0.7
34.356	2,2-Bis[4-[[4-chloro-6-(3-ethynylphenoxy)-1,3,5-triazin-2-yl]oxy]phenyl]propane	0.9
34.639	Stearic acid, 3-(octadecyloxy)propyl ester	0.7

As such, the reported relative concentrations of un-reacted phenol and other phenolic or non-phenolic compounds listed in Tables 2 and 3 were not the actual concentrations of these compounds in the liquid products tested. In future studies, other tools such as HPLC will be used for better and quantitative characterization of the

obtained liquid products. The formation of the phenolic compounds might be a result of the phenolysis/phenolation reactions between the added phenol solvent and the alkyl radicals derived from the proteins, fat and fiber components in the DDGS at a high temperature. The resulting liquid products, rich in phenol and phenolic compounds, may thus be a potential substitute for petroleum-derived phenol or an additive/modifier for the manufacturing of PF resin. The synthesis of PF resins using the DDGS-derived products will be considered in future work.

To examine the crystalline species in the crude DDGS sample and the solid residues from the liquefaction process, X-ray diffraction (XRD) measurements were carried out. Figure 7 illustrates the XRD patterns of the crude DDGS powder before and after liquefaction for 30 min in phenol at a temperature varying from 200°C to 450°C.
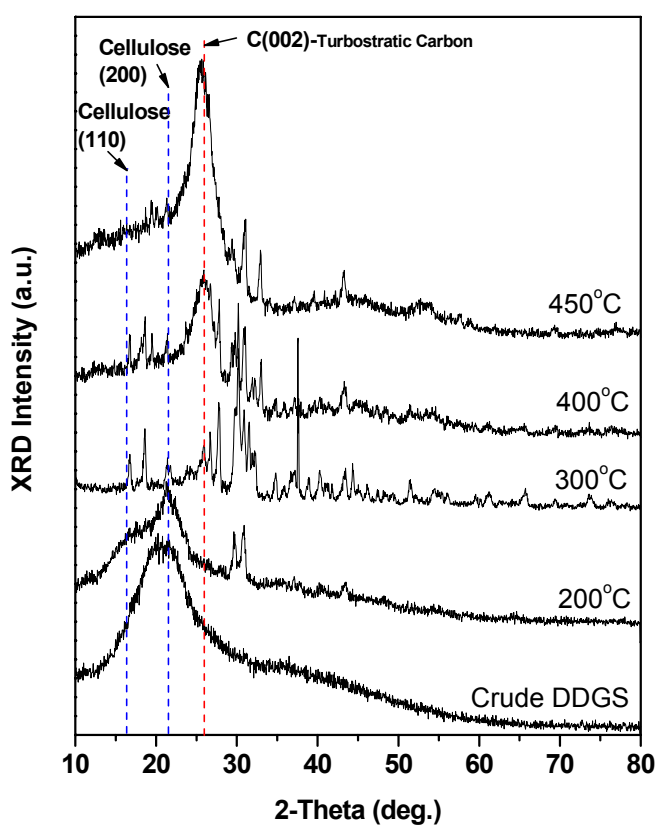

Fig. 7. X-ray diffraction patterns of DDGS powder before and after liquefaction in hot-compressed phenol (phenol/DDGS = 5/1) for 30 min at various temperatures.

The X-ray diffraction pattern of the crude DDGS showed a primary peak at $2\theta = 22.2°$ and a shoulder peak at $2\theta = 16.3°$, typical of cellulose-I. It has been well documented that these peaks correspond to the (200) and (110) planes of cellulose (Ishikawa et al. 1998; Borysiak and Doczekalska 2005). In the solid residue at 200°C, these cellulose-derived peaks weakened, while several strong XRD signals at $2\theta = 28°$ - $32°$ were detected, as shown in Fig. 7. These new peaks are likely due to the diffraction

lines of inorganic minerals in the DDGS, although the authors were not able to assign any compounds to these peaks due to the complexity of the inorganic minerals in the DDGS (as shown earlier in Table 1) and the possible reactions of the inorganic compounds during the liquefaction process. In the 300°C-sample, the diffraction lines of cellulose (110) and (200) planes both disappeared, suggesting a complete decomposition of cellulose and maybe the organic materials in the DDGS, which is in agreement with the result of the very low Solid yield (< 5wt%) at 300°C as shown earlier in Fig. 1. On the contrary, very strong signals of the inorganic minerals were detected in the 300°C sample. As the operation temperature increased to 400°C, a strong peak at $2\theta = 26°$, attributable to diffraction of C(002) for turbostratic carbon, was observed. This turbostratic carbon peak intensified drastically as the treatment temperature increased further to 450°C. The presence of these carbon diffraction lines in the solid residues at 400°C and 450°C suggests the formation of coke/char from the liquid intermediates/products due to the condensation reactions during the high-temperature liquefaction process, as evidenced by the liquefaction results in Fig. 1. Similar observations of crystalline carbon have also been reported in some previous studies on hydrothermal treatment of biomass or organic materials in near and supercritical water (Yu et al. 2004; Sharma et al. 2007). Figure 8 compares the XRD spectra of the resulting solid residues at 250°C for 5 min in phenol (phenol/DDGS = 1/1) with and without catalyst. In all the 250°C-sample, diffraction lines of cellulose, as well as the diffraction lines attributed to inorganic minerals, were the dominant signals, irrespective of whether a catalyst was present. A strong peak at $2\theta \approx 25°$ was detected in the solid residue from the treatment with the presence of NaOH catalyst. This peak might be attributed to the diffraction of mercerized cellulose formed in the NaOH treatment (Kasuya et al. 1997).

CONCLUSIONS

Efficient liquefaction of DDGS in hot-compressed phenol at 200-450°C was realized in the present work. The effects of treatment temperature, initial phenol/DDGS ratio, residence time, and catalysts on the yields of liquefaction products, as well as characterizations of typical liquid and solid products were investigated. The conclusions from this study may be summarized below:

1. Hot-compressed phenol proved to be a very effective solvent for liquefaction of DDGS, producing liquid products at a yield of >70 wt% for 30 min treatment at a temperature higher than 200°C without catalyst, where the phenol/DDGS ratio was fixed at 5/1. The Liquid yield attained a maximum of about 95 wt% at 300°C.
2. A higher initial phenol/DDGS ratio for the treatment produced a larger solid conversion and a greater yield of liquid products. The Liquid yield was less than 80 wt% in the treatment with a phenol/DDGS ratio of 1/1 at 300°C for 30 min, while it increased to about 95 wt% at a phenol/DDGS ratio of 5/1.
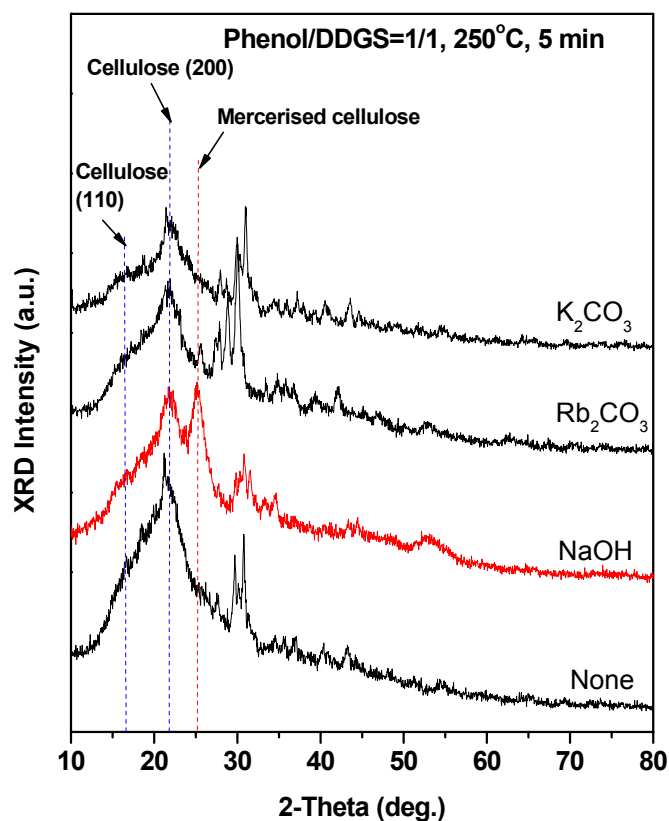
Fig. 8. X-ray diffraction patterns of DDGS powder before and after liquefaction in hot-compressed phenol (phenol/DDGS = 1/1) for 5 min at 250°C with various catalysts

3. Liquid yield appeared to reach a maximum of 97 wt% at 5 min for the DDGS liquefaction for the specified treatment conditions (i.e., Phenol/DDGS = 2/1 at 300°C). An increased residence time generally produced a lower yield of liquid products but a higher yield of solid residue, which was likely due to the increased coke/char formation from liquid intermediates/products during a prolonged residence time.

4. The presence of a catalyst of K_2CO_3, Rb_2CO_3, and NaOH in the treatment enhanced both the solid conversion and the Liquid yield. The catalytic effects were more evident at a higher temperature but appeared to level off at 300°C. At all temperatures tested, the catalysts for enhancing solid conversion and Liquid yield exhibited an activity sequence of $Rb_2CO_3 \approx K_2CO_3 >$ NaOH. The use of these catalysts resulted in 25% relative increase in the liquid yields for 5 min-operation with Phenol/DDGS of 1/1 at 300°C.

5. The GC/MS measurements for the DDGS-derived liquid products revealed high concentrations of un-reacted phenol, phenolic compounds/derivatives in the liquid products. The XRD results for the obtained solid residues suggested the formation of crystalline carbon from the treatment of DDGS at temperatures higher than 300°C.

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