Effects of Alternative Process Gases on the Thermochemical Conversion Process of Swine Manure

B. J. He, Y. Zhang, Y. Yin, T. L. Funk, G. L. Riskowski

ABSTRACT. *A thermochemical conversion (TCC) process was developed to convert swine manure into an oil product in a high temperature and pressure environment. The objective of this study was to examine the effects of different process gases, including CO, H_2, CO_2, N_2, and compressed air, on the efficiencies of oil production and waste reduction, and to explore the possibility of replacing costly reducing process gases, such as CO, with an inexpensive inert gas such as compressed air. It was found that the addition of a process gas to the reaction system before the experiment was critical for the TCC process to yield an oil product. Both reducing gases (such as CO and H_2) and inert gases (such as CO_2, N_2, and compressed air) can be used as a process gas. With the addition of reducing gases (i.e., CO and H_2), the process yielded a better quality oil product and achieved a higher oil production efficiency. There were no significant differences in the chemical oxygen demand reduction rate among the five process gases mentioned above. The pressurized process created by water vapor alone did not yield an oil product. It is unclear why the inert gases of N_2, CO_2, and compressed air affected the oil product formation from swine manure but water vapor did not.*

Keywords. Biomass, Renewable energy, Thermochemical conversion, Direct liquefaction, Swine manure.

A thermochemical conversion (TCC) process was developed to convert fresh swine manure into oil products at the University of Illinois at Urbana–Champaign as an exploration of an alternative process for swine waste treatment and renewable energy production. Traditionally, thermochemical conver–sion refers to any biomass depolymerization processes including pyrolysis, gasification, and direct–liquefaction. The major differences between pyrolysis and direct liquefaction are the operating conditions and end products. Pyrolysis is a thermal chemical decomposition of organic matter occurring in an oxygen absent or deficient environment. The primary products from the pyrolysis process are liquid and solid char. Usually, pyrolysis involves high temperature, an atmospheric or even a negative pressure, and a very short retention time. No reducing process gases, such as hydrogen or carbon monoxide, are necessary to be added to the pyrolysis process (White and Taiganides, 1971; Overend et al., 1986; Hayes, 1991; Bridgewater, 1994). Liquefaction is usually conducted in a high–temperature and high–pressure environment and liquid oil or tar is the major

product. A reductive gaseous reagent or a process gas is necessary to increase the oil yield and improve oil quality (Appell et al., 1980; Kranich, 1984; Chornet and Overend, 1985; Elliot et al., 1988; Datta and McAuliffe, 1993). The TCC process developed in our previous research belonged to the liquefaction because the reducing gas carbon monoxide was used as the process gas.

Based on 135 different experiments, 62.3% organic matter in the swine manure was converted into raw oil products under a high–temperature and high–pressure environment for a period of retention time. The COD (chemical oxygen demand) reduction efficiency was 64.5% based on 90 differ–ent experiments (He et al., 2000a). The effects of operating conditions, including the operating temperature, retention time, feedstock pH, and feedstock solids content, were also investigated. The experimental results showed that the operating temperature and retention time of the feedstock at the reaction temperature were the most important operating parameters. To achieve a high rate of COD reduction and oil production, the recommended operating temperature and retention time are 295–305°C and 15–30 minutes, respec–tively (He et al., 2000b). The feedstock pH and solids content also affected the process. High pH in the feedstock helped to increase the oil production rate, but the oil quality was not as good as that without pH control, i.e., with the natural pH of 6.1 for fresh swine manure. Ideally, the higher solids content in the feedstock, the better the efficiencies of oil production and waste reduction. However, if the solid content in the feedstock is higher than 25%, it is difficult to handle in such a process. Fresh swine manure with a total solids content of 20%–25% is suitable for the TCC process (He et al., 2000a,b). When the CO initial pressure increased from 0.34 MPa to 2.76 MPa, corresponding to a ratio of CO to volatile solids from 0.07 to 2.6 by weight, the oil production rate increased by about 10%. However, the COD reduction rate decreased by about 10% (He et al., 2001a). Therefore, a

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high CO initial pressure may not be desirable for the TCC process.

Many biomass liquefaction processes used either hydrogen or carbon monoxide as the reducing process gas. Researchers suggested numerous mechanisms to explain the function of the reducing gases. Not a single mechanism described the liquefaction process in general because of the complexity of the biomass feedstock compositions. However, it was generally accepted that a higher initial pressure of a reducing gas would help increase the oil product yields, even though the consumption of the reducing gas itself was a very small amount, or there was no consumption at all (Bestue–Labazuy et al., 1985). This reducing gas initial pressure sometimes was as high as 10.3 MPa (Boocock et al., 1980). When replacing hydrogen with helium to maintain an inert reaction environment and a constant operating pressure, Bestue–Labazuy et al. (1985) achieved an oil production efficiency of 35%. The oil production efficiency was 37% with hydrogen at an initial pressure of 4 MPa. It was concluded in their research that the initial process gas pressure had to be 4 MPa or higher. The initial observations in the thermochemical conversion of swine manure indicated that adding a process gas to the system was critical for the formation of an oil product and the process gas was not necessarily a reducing gas. Inert gases, e.g., CO_2 and N_2, had a function similar to that of reducing gases.

The objective of this study was to examine the effects of different process gases on the efficiencies of oil production and waste reduction, and to explore the possibility of replacing the costly reducing process gas, e.g., CO, with inexpensive gas such as compressed air.

MATERIALS AND METHODS

This study was carried out in a batch mode. The key apparatus was a 1.8–liter TCC reactor that could be operated at the extreme conditions of 375°C and 34.5 MPa. The TCC reactor was equipped with mechanisms for agitation, temperature monitoring and control, pressure monitoring, process gas introduction, and safety control. The operating parameters in the TCC process included operating temperature (T), retention time (RT), feedstock pH, process gas initial pressure (p_{ini}), and total solids content (TS). The fresh swine manure was collected biweekly from the partially slotted floor of a swine finisher room and stored at 4°C in a refrigerator. The solids content, pH, and COD of the manure samples were measured right after the samples were brought to laboratory. Elemental composition was measured monthly. The results showed that swine manure contained a relatively consistent total solids content of 27.4 ± 1.4% (mean ± SD by weight) and its natural pH was 6.06 ± 0.17 (mean ± SD). The elemental composition of the fresh swine manure is listed in table 1. The feedstock was processed directly without any pH adjustment throughout this study, i.e., at pH 6.1. The RT and TS were kept constant at 120 min and 20%, respectively. No extra catalysts were added to the system because of the presence of abundant minerals and carbonates, some of which, although unclear, played catalytic roles in the process. More detailed descriptions of the reactor system and the TCC process were reported previously by He et al. (2000a).

Table 1. Statistical characteristics of feedstock swine manure.

Elemental composition[a]	Mean ±st. dev.
Sulfur (S), ppm	3,816 ±608
Oxygen (O), %[b]	31.33
Nitrogen (N), %	3.45 ±0.38
Hydrogen (H), %	6.45 ±0.21
Carbon (C), %	45.67 ±1.12

[a] By weight on dry matter basis.
[b] By the difference: O = 100 – C – H – N – S.

The process gases investigated in this study included CO, CO_2, H_2, N_2, and compressed air. The air that occupied the reactor head space was replaced with a process gas before the experiment started. After the feedstock was charged into the reactor and all auxiliary parts were connected, a process gas, such as CO from a pressurized cylinder, was introduced into the reactor through a specified inlet to a pressure of 0.69 MPa. Then the reactor was switched to vent and the gas in the reactor was released. This procedure was repeated three times. After such a purging process, the amount of the residual free oxygen inside the reactor headspace was negligible. The reactor was then re–pressurized to the desired level with the process gas before the experiment began.

Solids analyses were performed on the oil products and post–processed water as described in the Standard Methods for the Examinations of Water and Wastewater (Clesceri et al., 1989). The chemical oxygen demand (COD) was measured using a colorimetric method developed by HACH for extremely high COD measurement (HACH Co., 1997). The benzene–soluble organic content, or the benzene solubles, in the TCC oil products was measured based on the ASTM Standard D4312–95a for petroleum products (ASTM, 1999). Elemental analyses were conducted on the feedstock and oil products for carbon (C), hydrogen (H), nitrogen (N), and sulfur (S). Carbon, hydrogen, and nitrogen were detected by a CHN analyzer (Model CE440 by Exeter Analytical, Inc. N. Chelmsford, Mass.). Sulfur analysis was performed on an Inductively Coupled Plasma (ICP) instrument (Perkin Elmer, Norwalk, Conn.).

The criteria for determining process gas effects were oil production efficiency, benzene solubles, and COD reduction efficiency. Oil production rate was used to measure the TCC process efficiency. Benzene solubles of the oil products were used as an indicator of the oil quality. Elemental compositions (CHNS) were also used to characterize the oil products. The waste strength of the swine manure slurry was characterized by its COD and the relative change in COD from feedstock to the post–processed water was used as the measure of the waste reduction efficiency. The raw oil production efficiency, benzene solubles of the TCC oil products, and COD reduction efficiency are defined as follows:

$$\text{Oil production efficiency (\%)} = \frac{\text{total oil product (g)}}{\text{total volatile solids input (g)}} \times 100\% \qquad (1)$$

$$\text{Benzene solubles (\%)} = \left(1 - \frac{\text{solid residue (g)}}{\text{total oil sample (g)}}\right) \times 100\% \qquad (2)$$

$$\text{COD reduction efficiency (\%)} =$$

$$(1 - \frac{\text{COD of post} - \text{processed water}}{\text{COD of raw manure}}) \times 100\% \qquad (3)$$

RESULTS AND DISCUSSION

INITIAL OBSERVATIONS

Theoretically, either hydrogen or carbon monoxide could help maintain a reductive environment in a liquefaction system, which is necessary for the decarboxylation and hydrogenation reactions to occur. Inert gases would not help by any means on the biomass conversion process. Initial observations showed, however, that inert gases such as nitrogen did affect the TCC process as summarized in table 2.

When carbon monoxide was used as the process gas at an initial pressure of 0.69 MPa, the two experiments yielded 38.3% and 54.2%, respectively, of oil products. When the CO initial pressure was 1.4 MPa, the oil production efficiency was 59.2%. If half of the initial CO was replaced by N_2 and the total initial pressure was maintained at 1.38 MPa, the oil production efficiency was 45.2%, at similar level as when CO only was used at 0.69 MPa initial pressure.

When the CO initial pressure was kept at 0.69 MPa and the total initial pressure increased to 1.93 MPa, the oil production efficiency was 53.9%, which was essentially at the same level as that with CO as the only process gas with an initial pressure of 0.69 MPa. If both the CO and N_2 initial pressures were doubled and the total initial gas pressure was 2.76 MPa, the oil production efficiency remained at the same level as when only CO was used at 0.69 MPa. In the above two conditions, the oil production efficiency, benzene solubles of the oil products, elemental composition, and the COD reduction efficiency were basically the same. To further investigate the N_2 effect, two runs were performed with N_2 as the only process gas. The N_2 initial pressures were the same as the CO tests (~1.3 MPa) and the total operating pressures were about 8 MPa. The results showed that the oil production efficiency was lower but not significantly different from that with CO as the process gas. When the nitrogen initial pressure was further reduced to 0.34 MPa, no oil was produced at this operating temperature (285°C), a similar phenomenon as observed for CO as process gas only (He et al., 2001a). It was found that there was no significant difference between the elemental compositions and the COD reduction rates were essentially at the same level in these preliminary results.

One question was raised: What was the function of the inert nitrogen in the process? Under the operating conditions employed, an inert gas was not expected to participate in the depolymerization and oil formation reactions. Another fact was that the initial nitrogen pressure had to be 0.69 MPa or higher for the process to yield an oil product. Was it a matter of total operating pressure? Two experiments were carried out without adding initially any process gases. The operating pressure was created solely by the water vapor that was in equilibrium with the liquid water in the feedstock slurry. The results showed that no oil was produced even when the operating temperature was raised to 305°C and the total corresponding operating pressure was 9.4 MPa, which was even higher than that with a 1.3 MPa N_2 initial pressure. It was apparent that a process gas, either reducing or inert, must be added to achieve an oil product. The above observations encouraged us to further explore the effects of different process gases, including reducing gases such as CO and H_2, and inert gases such as N_2, CO_2, and compressed air, on the TCC process.

NITROGEN AS THE PROCESS GAS

The results of the temperature effect on oil yield, benzene solubles, and COD reduction efficiency when N_2 was used as the process gas are summarized in figure 1. Each data point in figure 1 represents the average of two or three replications. Experimental results showed that the process did not substantially produce an oil product until the operating temperature reached 285°C. When the operating temperature increased to 295°C, the oil production efficiency reached its highest point, 68.5%. When the operating temperature was 295°C or higher, the oil production efficiency started to decrease as the operating temperature increased. At the highest operating temperature explored (315°C), the oil production efficiency dropped to 62%. The benzene solubles decreased constantly as the operating temperature increased from 275°C to 315°C, from 77% to 71%, indicating that the increase of the operating temperature affected the benzene solubles negatively. The operating temperature did not significantly affect the COD reduction efficiency, which

Table 2. Effect of nitrogen addition on the TCC process. Operating conditions other than those listed: temperature 285°C, retention time 120 min, and feedstock pH = 6.1.

Experiment	Initial pressure		Operating pressure (MPa)	Oil product					COD reduction (%)
	CO (MPa)	N_2 (MPa)		Prod. efficiency (%wt)	Benzene solubles (%wt)	C (%wt)	H (%wt)	N (%wt)	
1	0.69	0.0	7.8	38.3	83.7	63.1	9.4	5.8	63.9
2	0.69	0.0	7.9	54.2	82.7	67.5	9.1	3.9	56.6
3	1.38	0.0	7.6	59.2	83.1	71.2	9.0	4.1	61.7
4	0.69	0.69	8.1	45.2	77.7	68.3	9.2	4.7	68.2
5	0.69	1.24	8.4	53.9	76.3	70.6	9.2	4.9	68.5
6	1.52	1.24	10.2	52.7	77.9	65.2	9.1	4.4	65.5
7	0.0	1.30	8.0	49.6	70.2	70.8	9.3	5.8	63.8
8	0.0	1.24	8.1	48.8	71.2	70.9	8.9	5.7	63.9
9	0.0	0.69	7.8	32.7	66.9	74.9	9.6	7.1	68.8
10	0.0	0.34	7.3	0.0	n/a[b]	n/a	n/a	n/a	71.2
11	0.0	0.0	7.2	0.0	n/a	n/a	n/a	n/a	67.0
12	0.0	0.0	9.4[a]	0.0	n/a	n/a	n/a	n/a	72.5

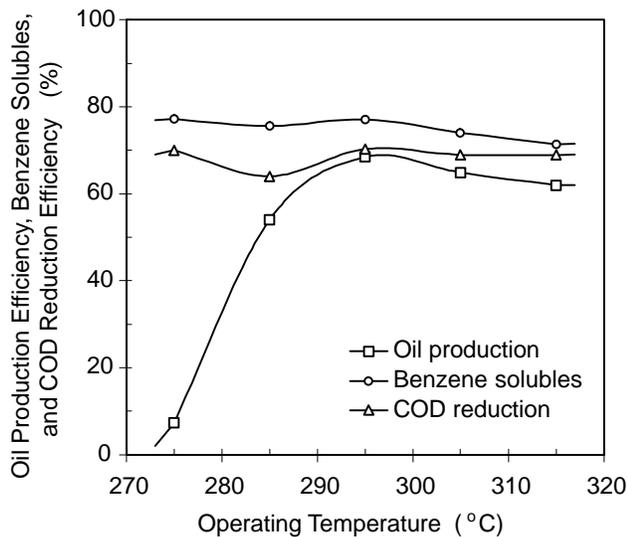[a] Operating temperature was 305°C.
[b] n/a = not analyzed.

Figure 1. Effect of operating temperature on oil production, benzene solubles, and COD reduction with nitrogen as the process gas. The operating conditions were: N_2 initial pressure p_{ini} = 0.69 MPa, TS = 20%, RT = 120 min, and feedstock pH = 6.1. The corresponding operating pressures were 6.7~11.5 MPa.
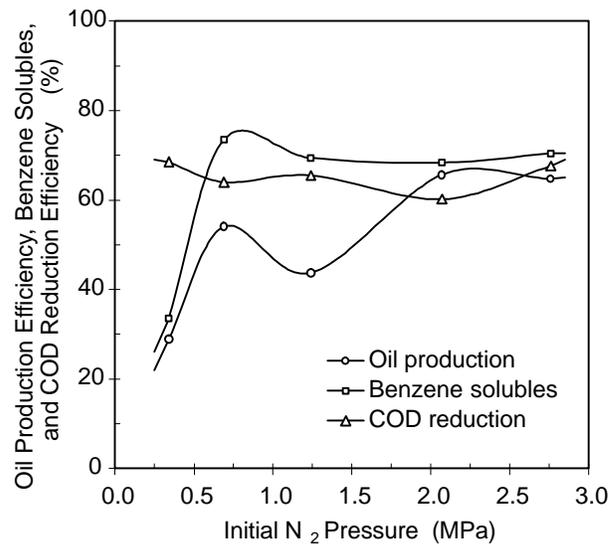

Figure 2. Effect of initial pressure on oil production, benzene solubles, and COD reduction with nitrogen as the process gas. The operating conditions were: T = 285°C, TS = 20%, RT = 120 min, and feedstock pH = 6.1. The corresponding operating pressures were 7.4 ~10.9 MPa.

stayed at about 69% throughout the operating temperature range. The COD of the post–processed water remained unaffected. Compared to the results with CO as the process gas, the COD reduction efficiency with N_2 as the process gas was at the same level (He et al., 2001a).

The nitrogen initial pressure affected the production efficiency and benzene solubles of the oil products. It needed to be high enough to achieve a substantial oil yield as shown in figure 2. Each data point in figure 2 represents the average of two or three replications. When the N_2 initial pressure was lower than 2.1 MPa, the oil production efficiencies were lower than 60% and the fluctuation was high (10% to 20%). When the N_2 initial pressure was 2.1 MPa, the oil production efficiency reached 65% and remained at the same level when the N_2 initial pressure increased to 2.7 MPa. The benzene solubles had a great increase as N_2 initial pressure increased from 0.34 MPa to 0.69 MPa. It then decreased to 69% and stayed about constant thereafter when the N_2 initial pressure increased from 1.24 MPa to 2.76 MPa. The N_2 initial pressure had an insignificant effect on the COD reduction efficiency. When the N_2 initial pressure increased from 0.34 MPa to 2.07 MPa, the COD reduction efficiency slightly decreased from 68.6% to 60.2%; then it came back up to 67.6% as the N_2 initial pressure increased to 2.76 MPa. This is different from that when CO was used as the process gas, where the COD reduction efficiency had a large decrease when the CO initial pressure increased from 2.07 MPa to 2.56 MPa (He et al., 2001a).

Apparently, nitrogen was involved to some extent in the biomass conversion process. This is contradictory to the hypothesis that nitrogen was an inert gas and therefore it would not participate in any depolymerization reactions. Possible explanations of the phenomena observed remain unknown to the authors.

CARBON DIOXIDE AS THE PROCESS GAS

Carbon dioxide is a by–product of the TCC process. In principle, the addition of CO_2 to the biomass conversion

process would prevent the depolymerization process from yielding an oil product. Experiments showed, however, that the addition of CO_2 had a similar effect on the process as N_2 did. The process did not succeed in yielding an oil product in every run when the operating temperature was lower than 275°C (fig. 3). Each data point in figure 3 represents the average of two or three replications. The oil production efficiency increased to about 59% as the operating temperature reached 285°C, and it further increased to 62% at 295°C. The oil production efficiency, however, decreased gradually from 62% to 57% when the operating temperature increased to 315°C. The benzene solubles constantly increased from 65% at 275°C to about 75% at 315°C. This increase indicates that increasing the operating temperature affected the benzene solubles positively. The operating temperature also affected the COD reduction efficiency. It increased constantly from 64% at 275°C to 71% at 305°C, but dropped to 67% at 315°C.

The effects of CO_2 initial pressure on the process are shown in figure 4, where each data point represents the average of two or three replications. As the CO_2 initial pressure increased from 0.34 MPa to 1.24 MPa, the oil production efficiency increased greatly, from less than 40% to 64%. When the CO_2 initial pressure was above 1.24 MPa, the increasing trend of oil production efficiency slowed down. The oil production efficiency was more than 70% when the CO_2 initial pressure increased to 2.7 MPa. This phenomenon was similar to that of N_2 as the process gas. On the other hand, the CO_2 initial pressure did not affect the benzene solubles of the oil product. The benzene solubles remained virtually constant at 70% throughout the CO_2 initial pressure range. This reflects the inert characteristics of carbon dioxide, which presumably did not participate in any reactions involving oil formation. Therefore, increasing the CO_2 initial pressure would not affect the COD reduction efficiency significantly either. It showed that the COD reduction efficiency remained at the same level (67%) as when N_2 was added.
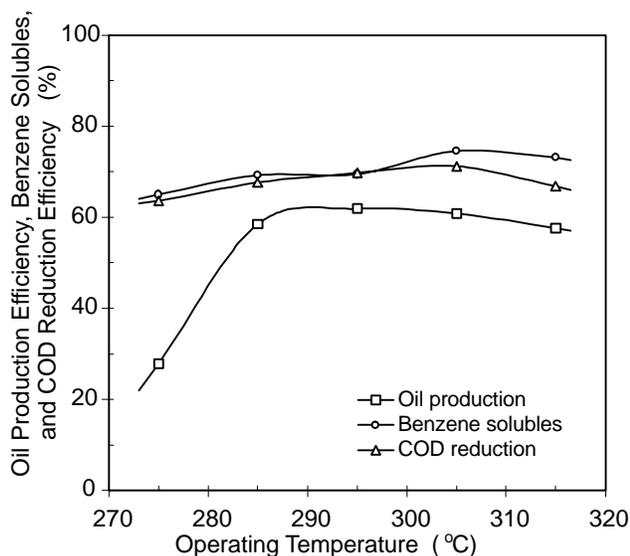
Figure 3. Effect of operating temperature on oil production, benzene solubles, and COD reduction with CO₂ as the process gas. The operating conditions were: CO_2 initial pressure p_{ini} = 0.69 MPa, TS = 20%, RT = 120 min, and feedstock pH 6.1. The corresponding operating pressures were 6.7~11.5 MPa.
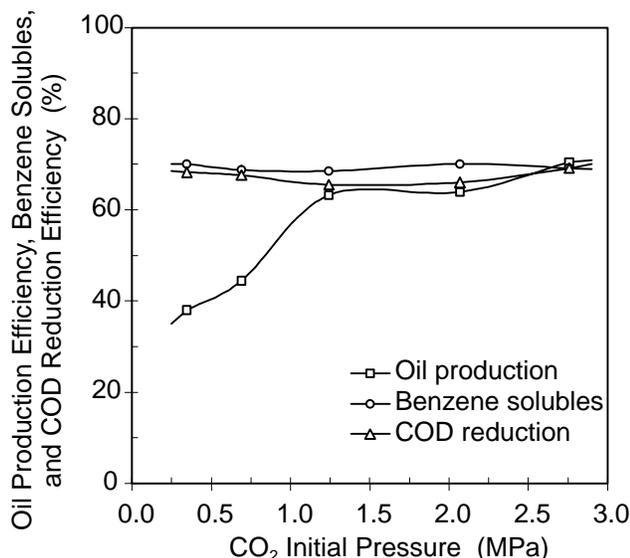

Figure 4. Effect of initial pressure on oil production, benzene solubles, and COD reduction with CO₂ as the process gas. The operating conditions were: T = 285°C, TS = 20%, RT = 120 min, and feedstock pH = 6.1. The corresponding operating pressures were 7.4~10.4 MPa.

HYDROGEN AS THE PROCESS GAS

Hydrogen is another commonly used reducing gas in the biomass thermal liquefaction process. The application of H_2 serves a dual purpose. First, it is a reductive reagent, like CO, which reduces the oxidative compounds depolymerized from biomass to oil. Secondly, hydrogen itself is a high energy–containing element and one of the two key elements in hydrocarbons. Theoretically, introducing H_2 to the liquefaction process would benefit high quality oil product formation. The drawback is the high operating cost if H_2 is involved. When H_2 was used as the reducing gas, the operating temperature was usually higher than that with CO as the process gas because of its low reactivity at low temperatures.

In this study, the operating temperature range was from 265°C to 335°C and the corresponding operating pressures were 5.2 to 15.2 MPa.

The operating temperature must be 275°C or higher for the process to yield an oil product (fig. 5). Each data point in figure 5 represents the average of two or three replications. The oil production efficiency decreased from 75% to 64% and benzene solubles increased from 66% to 96% when the operating temperature changed from 275°C to 335°C. The high value of benzene solubles indicated that the oil quality was greatly improved as the temperature increased. The oil production efficiency was high at 305°C. This phenomenon may indicate that it was close to the optimum temperature that favors oil formation when using H_2 as the process gas.

As mentioned frequently in the literature, the initial H_2 pressure for a liquefaction process must be high enough to allow a successful process, which could be as high as 10 MPa (Boocock et al., 1980). In this study, the initial H_2 pressure could be as low as 0.34 MPa to yield an oil product although the oil production efficiency was low at this initial pressure. When the H_2 initial pressure increased to 0.69 MPa, the oil production efficiency increased above 60%. The oil production efficiency tended to increase until the H_2 initial pressure was 2.1 MPa. When the pressure was increased to 2.7 MPa, the oil production efficiency unexpectedly decreased from 76% to 67% (fig. 6). Each data point in figure 6 represents the average of two or three replications. The H_2 initial pressure affected benzene solubles of the oil products slightly. The benzene solubles gradually increased from 70% to 74% as the H_2 initial pressure increased from 0.34 MPa to 1.24 MPa, and decreased slowly from 74% to 69% as the H_2 initial pressure increased above 1.24 MPa. Increasing the H_2 initial pressure did not benefit the benzene solubles as much as increasing the operating temperature.

The H_2 initial pressure affected the COD reduction efficiency negatively (fig. 6). When the H_2 initial pressure increased from 0.34 MPa to 2.1 MPa, the COD reduction efficiency decreased from 69% to 62%. When the H_2 initial
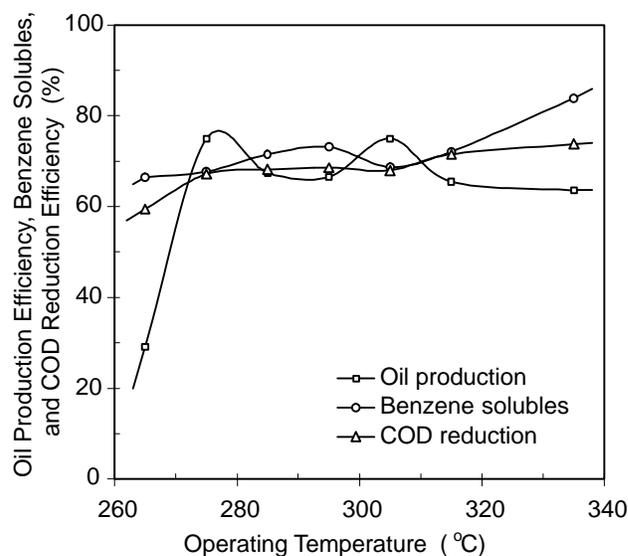

Figure 5. Effect of operating temperature on oil production, benzene solubles, and COD reduction with hydrogen as the process gas. The operating conditions were: H_2 initial pressure p_{ini} = 0.69 MPa, TS = 20%, RT = 120 min, and feedstock pH = 6.1. The corresponding operating pressures were 5.2~15.2 MPa.
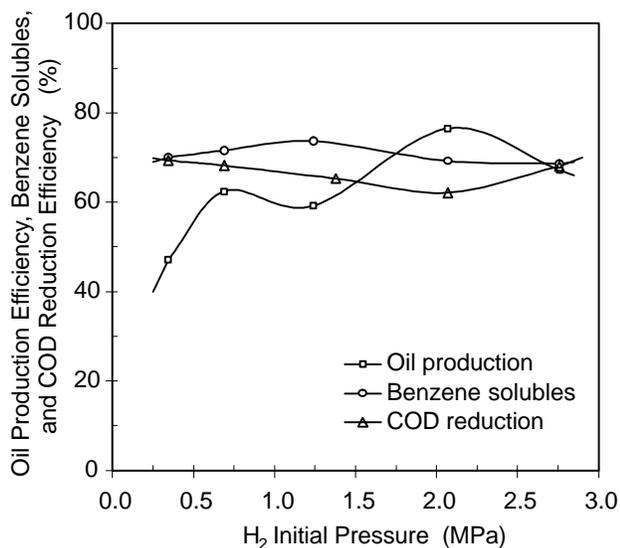
Figure 6. Effect of initial pressure on oil production, benzene solubles, and COD reduction with hydrogen as the process gas. The operating conditions were: T = 285°C, TS = 20%, RT = 120 min, and feedstock pH = 6.1. The corresponding operating pressures were 7.5~10.5 MPa.
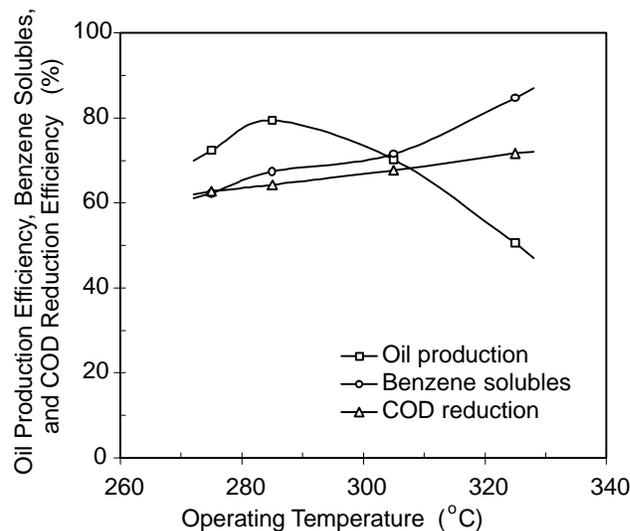

Figure 7. Effect of operating temperature on oil production, benzene solubles, and COD reduction with compressed air as the process gas. The operating conditions were TS 20%, RT 120 min, and feedstock pH 6.1. The corresponding operating pressures were 6.2~13.4 MPa.

pressure was 2.7 MPa, the COD reduction efficiency was back up to 67%. This phenomenon corresponded to the change in oil production efficiency, which also dropped sharply. However, the cause of the oil production efficiency decrease was not clear. The reason that the H_2 initial pressure had a negative effect on the COD reduction efficiency was similar to that of the CO effect on the COD reduction efficiency, i.e., the reductive environment created by the high H_2 pressure prevented the organic compounds from deep oxidation and led to the high COD in the post–processed water (He et al., 2001a).

COMPRESSED AIR AS THE PROCESS GAS

As observed in preliminary tests, the addition of a process gas, even an inert gas, was necessary for the TCC process to form an oil product. Compressed air was found affecting the oil production efficiency as nitrogen did. At low operating temperatures (275°C~285°C), the oil production efficiency was as high as 80%, as shown in figure 7 where each data point represents the average of two or three replications. When the temperature increased from 285°C to 325°C, the oil production efficiency sharply decreased from 80% to 50%. The sharp decrease of the oil production efficiency was probably caused by the oxidization of carbonaceous matters to CO_2 in the presence of free oxygen. Benzene solubles of the oil products increased constantly as the operating temperature increased. At 275°C, the benzene solubles were 62%. This low value of benzene solubles corresponded to the high oil production efficiency at this temperature. The high oxygen content in the oil products resulted in the high oil production efficiency. When the operating temperature reached 325°C, the benzene solubles increased to 85%. The benzene solubles were at essentially the same level as when CO was used as the process gas at the same operating temperature (He et al., 2000b, 2001a).

The initial pressure effects of compressed air on the oil production efficiency and benzene solubles were investigated in a relatively narrow range (fig. 8). The pressures of the compressed air were 0.34~1.24 MPa. At a low initial

pressure of 0.34 MPa, the oil production efficiency was 67%. It increased to 80% when the initial air pressure increased to 0.69 MPa. When the initial air pressure was further increased, the oil production efficiency fluctuated in the range of 63% to 82% wt, with an average of 72.8%. This means that adding more air to the system would not benefit the oil production efficiency. Using compressed air as the process gas did not affect the benzene solubles significantly in the pressure range tested. The benzene solubles were in the range of 64% to 67%, which is much lower than that with CO as the process gas, and even lower than with N_2 and CO_2 as the process gases. The initial pressure of the compressed air apparently did not affect the COD reduction efficiency of the process. The COD reduction efficiency stayed basically at the same level of 63%.
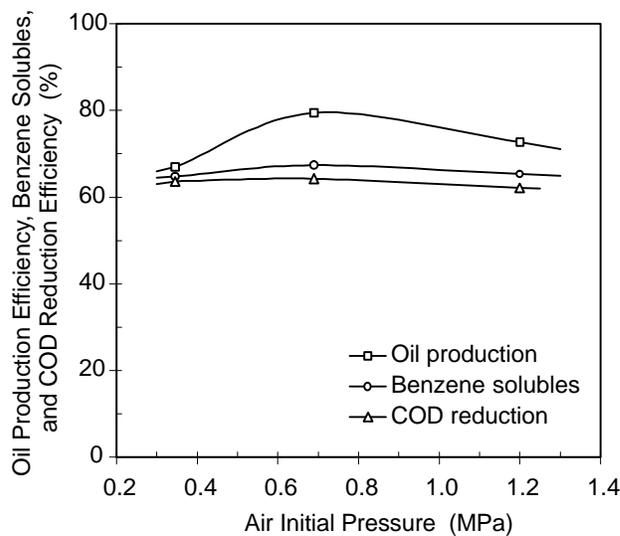

Figure 8. Effect of initial air pressure on oil production, benzene solubles, and COD reduction. The operating conditions were: 285°C, TS = 20%, RT =120 min, and feedstock pH = 6.1. The corresponding operating pressures were 7.1~7.5 MPa.

COMPARISONS OF OIL PRODUCTION AND COD REDUCTION

The experimental results of adding different process gases at 305°C on the oil production are summarized in table 3. It is shown that the oil production efficiencies varied by 20% from the highest with H_2 as process gas to the lowest with CO as the process gas. When carbon monoxide was the process gas, the oil production efficiency was 57.1% with a standard deviation of 8.4%. When the N_2 and CO_2 were used as the process gases the oil production efficiencies were 64.9% and 60.8%, respectively. The oil production efficiency reached its highest point when H_2 was used as the process gas. It was 77.7% with a standard deviation of 0.7% wt. The oil production efficiency with compressed air as the process gas was 70.2%, the second–highest yield among the five. The oil quality (indicated by the benzene solubles) was quite different with the different process gases. Contrasted to oil production efficiency, the highest benzene solubles occurred when CO was added as the process gas (88.6% with a standard deviation of 1.6%). The benzene solubles with other process gases ranged from 68.7% to 78.6%. Statistically, they are not significantly different from each other. The benzene solubles of the oil products were affected more by CO than by any other process gas at 305°C.

The oxygen content of the oil products, another indicator of oil quality, varied considerably. The highest oxygen content was 15.2% when CO_2 was added. This occurred because adding CO_2 did not create a reductive atmosphere in the reaction system. Although an oil product was formed, the oxygen elimination process was hindered by the high partial pressure of CO_2. When the reducing gases CO and H_2 were added, the oxygen content was the lowest, 7.7% and 6.7%, respectively. With N_2 and compressed air as the process gases, the oxygen contents were 9.4% and 10.3%, respectively. The oxygen content affected the energy value of the oil products. Higher oxygen content lowered the heating value thus lowered the oil quality. Therefore, the oil products with CO and H_2 as process gases had better quality with low oxygen content.

The COD reduction efficiency varied slightly among the experiments with different process gases. The highest COD reduction efficiency was 71.2% when CO_2 was added, and the lowest was 64.8% when compressed air was added. The relative difference between the highest and the lowest COD reduction efficiencies was less then 10%. The COD reduction efficiencies with the additions of the remaining three gases were approximately the same (about 68%). Considering the variations with the additions of different gases, the COD reduction efficiencies were essentially the same for all five situations. In other words, the use of different process gases had little effect on the COD reduction efficiency.

CONCLUSIONS

It was concluded from this study that the addition of a process gas, either reducing gases such as CO and H_2 or inert gases such as N_2, CO_2, and compressed air, was necessary for the TCC process to yield an oil product. High operating pressures created by water vapor under high temperatures did not lead to oil formation. Nitrogen and carbon dioxide affected the biomass conversion process and had a similar effect on the oil production efficiency as CO did. The oil quality with inert gases of N_2 and CO_2 was lower than that with reducing gases of CO and H_2 as indicated by the low benzene solubles and high oxygen content in the oil products. The process yielded an oil product when compressed air was used as a process gas, but the quality of the oil was poor. The COD reduction efficiencies were virtually the same among the process gases tested.

Table 3. Comparison of the different process gases on the TCC process. The operating conditions were 305°C, RT = 120 min, TS = 20%, initial pressure of process gas p_{ini} = 0.69 MPa, feedstock pH = 6.1. The corresponding operating pressure was 10.5 MPa. The error terms are standard deviations. The results (in rows) of treatment A were significantly different from treatment B at the 95% confidence level for the mean.

Effects on TCC process	Process gases				
	CO	N_2	CO_2	H_2	Air
Oil production efficiency (%)	57.1±8.3[B]	64.9±6.4[B]	60.8±8.0[B]	77.7±0.7[A]	70.2±5.0[B]
Benzene solubles (%)	88.6±1.6[A]	74.1±6.6[B]	74.6±7.2[B]	68.7±7.2[B]	71.5±3.8[B]
COD reduction efficiency (%)	68.4±1.8[B]	67.4±6.9[B]	71.2±0.9[B]	67.9±1.8[B]	64.8±3.0[B]
Oxygen in TCC oil (%)	7.7±1.3[B]	9.4±0.1[B]	15.2±0.5[A]	6.7±0.8[B]	10.3±0.7[B]

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