

OPERATING TEMPERATURE AND RETENTION TIME EFFECTS 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) reactor was developed to process swine manure for waste reduction and energy production. The operating temperature and retention time are the two key parameters affecting the process. Carbon monoxide (CO) was employed as the reductive reagent. The investigated ranges of the operating temperature and retention time were 275°C ~ 350°C (corresponding operating pressures were 7 ~ 18 MPa) and 5 ~ 120 min, respectively. The pH value of the fresh swine manure (pH= 6.1), CO to VS ratio (CO:VS = 0.07 by weight or CO initial pressure p_{ini} = 690 kPa), and total solids content (TS = 20%) were kept constant for all the experiments in this study. No extra catalyst was added in the experiments because of the presence of plentiful minerals and carbonates. The operating temperature was the most important factor affecting the TCC process. No substantial oil product yield was achieved unless the temperature reached 285°C or above. Temperature higher than 335°C led to solid char formation. Retention time affected the completeness of the TCC process. The retention time for achieving high oil yield and quality was largely dependent upon the operating temperature levels. The suggested operating temperature and retention time for the TCC process are 295°C to 305°C and 15 to 30 min, respectively.

Keywords. Swine manure, Manure utilization, Biomass energy, Thermochemical conversion, Direct liquefaction.

A thermochemical conversion (TCC) process of swine manure as an alternative means of waste treatment and utilization was developed and tested. The detailed description of the TCC process was presented by the authors previously (He et al., 2000). Results showed that the TCC process could not only substantially reduce the waste strength of swine manure slurry but also produce renewable energy. The end products of the process include raw TCC oil, post-processed water, gases, and solid residues.

Ligno-cellulosic wastes can be converted to various forms of energy through numerous TCC processes, depending upon the characteristics of the raw materials and the type of product desired. Among the TCC processes, liquefaction was one of the most widely studied (Minowa et al., 1995; Datta and McAuliffe, 1993; Gharieb et al., 1993; Meier and Rupp, 1991; Chornet and Overend, 1985; Kranich, 1984; Kaufman and Weiss, 1975). Liquefaction was historically linked to hydrogenation and other high-pressure thermal decomposition processes of coal. In such a liquefaction process, hydrogen (H₂) or carbon monoxide (CO) was usually employed as a reductive reagent to eliminate the oxygen element and convert the carbonaceous materials to liquefied products through a complex sequence of changes in physical

structure and chemical bonds, hence, to increase the oil product yield and improve the oil quality (Chornet and Overend, 1985; Datta and McAuliffe, 1993; Appell et al., 1980). One pivotal study of such liquefaction processes was done in the 1970s funded by the Bureau of Mines of the United States (Appell et al., 1980). Appell et al. investigated a TCC process to convert cellulosic wastes, including manure, to oil. In their study, the operating conditions were 350 ~ 400° C and 27.5 ~ 41.2 MPa. Carbon monoxide (CO) and hydrogen were used as the process gases. Reactions were carried out in the presence of sodium carbonate as catalyst. The results showed that the conversion efficiency of volatile solids was 90% or better and the oil yields varied from 40% to 50%. They found that the presence of CO heavily affected the organic matter conversion rate and the oil yield. Addition of hydrogen was not as effective as that of carbon monoxide. According to Appell et al., the presence of some liquid water is desirable. Without sufficient liquid water, the TCC process would likely convert the organic matter into a solid char rather than liquid oil.

Research and development activities of biomass thermochemical conversion processes at pilot and commercial scale have been conducted in the U.S. since the 1970s. The National Renewable Energy Laboratory (NREL) has set up a biofuels program to promote R&D in this area (Mielenz, 1996). A commercial Biomass Gasification Facility (BGF) in Paia, Hawaii, has a capability of gasifying over 100 tons/day of biomass (Trenka, 1996). Another project is the Vermont commercial demonstration of biomass gasification. It has over 20,000 h of successful operation at Battelle Columbus Labs process research unit (PRU), and features the first U.S. demonstration of a gas turbine operating on fuel gas produced by the thermal gasification biomass (Farris and Weeks, 1996). The NREL currently maintains an intense research program on biomass

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conversion. To the best of our knowledge, there is no commercial or pilot scale direct liquefaction facility in operation using animal manure as feedstock.

Swine manure is one type of biomass. Although its composition widely depends on many different factors such as the feed ration, animal age, and storage time, the major organic components in swine manure include glucose, cellulose, hemicellulose, and lignin (Hrubant et al., 1978). In terms of elemental composition, carbon, and hydrogen account for approximately 50% by dry weight basis (Zahn et al., 1997). This portion of carbon and hydrogen could be converted to an applicable renewable energy form, such as oil product. As presented previously, the thermochemical conversion process of swine manure converted 63% of volatile solids to an oil product and the COD reduction rate was 70% (He et al., 2000). To optimize the TCC process, the operating parameters including temperature, retention time, process gases, feedstock pH, and solids content were systematically investigated. This article is the first part of this study and presents the experimental results of operating temperature and retention time effects. The objective was to examine the effects of operating temperature and retention time on the oil production and chemical oxygen demand (COD) reduction efficiencies.

MATERIALS AND METHODS

A TCC batch reactor previously developed was employed to study the operating temperature (T) and retention time (RT) effects on the process. Other operating parameters, e.g., CO initial pressure, pH, and solids content of the feedstock, were kept constant throughout this study. The process setup and control scheme, procedures of the analyses and measurements, and results were described and discussed in previous studies (He et al., 2000). Fresh swine manure was collected from the floor of finisher swine rooms. The elemental and solids analysis results showed that the characteristics of the swine manure, such as carbon and hydrogen content, volatile solids, and pH value, were consistent throughout the study. The results of the feedstock analyses are summarized in table 1. The swine manure was adjusted with tap water to an experimental total solids content of 20% and remained constant for all the experiments in this study. The pH value of the fresh swine manure was 6.1 and it was not adjusted. Carbon monoxide was used as the process gas. It was introduced into the TCC reactor at 690 kPa, the corresponding CO to volatile solids ratio (CO:VS) was 0.07:1 (by weight), before the operation. Because of the presence of abundant minerals and carbonates, no extra catalyst was added throughout the experiments.

The oil product was separated by gravity from the post-processed water after the run. Samples of the oil product were analyzed for its elemental composition such as carbon, hydrogen, nitrogen, and sulfur, the solubles in benzene, and ash content. Other properties such as viscosity, thermogravimetric analysis, and heating value were also characterized preliminarily (Yin et al., 2000). Further characterization of the oil product and its possible utilization need to be explored in future study. The post-processed water was sampled and analyzed for COD and solids contents. Nutrient value analysis performed for some samples of the post-processed water showed that the

Table 1. The characteristics of feedstock swine manure used in this study

Group/specific	Mean \pm SD
Solids content	
Total solids (TS) (%)	27.43 \pm 1.35
Volatile solids (VS) (% of TS)	87.28 \pm 1.27
Fixed solids (FS) (% of TS)	12.72 \pm 1.27
Elemental composition (dry basis)	
Carbon (%)	45.67 \pm 1.12
Hydrogen (%)	6.45 \pm 0.21
Nitrogen (%)	3.45 \pm 0.38
Sulfur (%)	0.38 \pm 0.06
Oxygen* (%)	31.33
pH	6.06 \pm 0.17
COD (mg/L)	325 200 \pm 2000

* By the difference: O = 100 - C - H - N - S - FS.

nutrient level is still too high to discharge it to a wastewater stream. Research is initiated to further study the treatment and application of the post-processed water.

The criteria to determine the operating parameter effects were the oil product yield, benzene solubles of the oil product, content of carbon and hydrogen, and waste or COD reduction efficiency. The feedstock, swine manure slurry, was completely converted into different products: raw TCC oil, post-processed water, solid residues, and gases. The conversion rate of volatile solids in feedstock through this process was 100%. Therefore, conversion rate was not considered as a process parameter in other biomass conversion processes. Oil product yield was used as one measure of the TCC process efficiency. Benzene solubles of the oil product was used as an indicator of the oil quality. Based on the chemistry principle of "like dissolves like", higher solubles of the oil product in an organic solvent indicates that the oil product contains more hydrocarbon-like components, thus has better oil quality. High carbon and hydrogen contents in the oil product are desirable. Carbon and hydrogen contents in the oil product and the molar ratio of hydrogen to carbon (H:C) were the other indicators used to present the oil quality. The relative difference of the CODs in swine manure slurry and in the post-processed water after the TCC process was used as the measure of waste reduction efficiency.

RESULTS AND DISCUSSION

OPERATING TEMPERATURE EFFECT

Operating temperature is the most important factor in the TCC process and was used as the primary control parameter. When the TCC reactor was heated, a liquid-vapor equilibrium was established between the liquid and its vapor in this closed system. The operating pressure was then coupled with the operating temperature through the saturated water vapor corresponding to that specified temperature. Therefore, the control of operating temperature is also indirectly the control of the operating pressure. Figure 1 depicts the effect of the operating temperature on the oil product yield and its solubles in benzene. Each data point in figure 1 represents the average of two or three replications. It is seen that no substantial oil product was yielded when the temperature was below 285°C. When the temperature increased to 285°C, the oil product yield was increased to 56.9% of the total VS input with a standard deviation of 5.7%. As the temperature

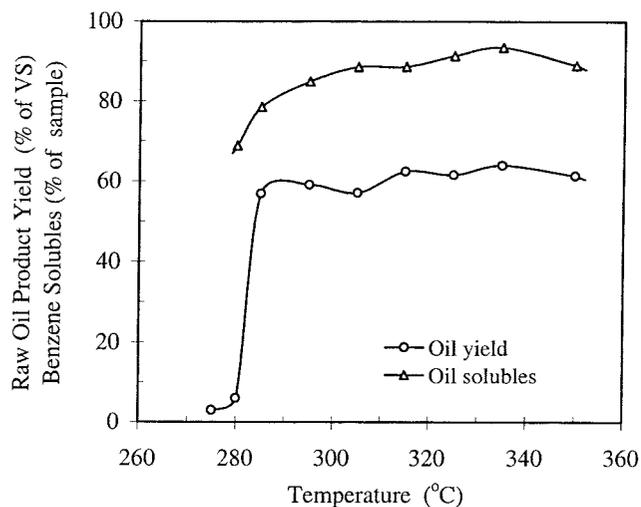


Figure 1—Temperature effect on the oil product yield and its benzene solubles. The operating conditions were CO:VS = 0.07 (wt) or p_{ini} = 690 kPa, RT = 120 min, TS = 20%, and feedstock pH = 6.0. The corresponding operating pressures were 7–18 MPa.

increased from 285°C to 335°C, the oil product yields increased slowly, from 57% to 64%. When the temperature was raised to 350°C, the oil yield experienced a drop back to 60%. The benzene solubles of the oil product followed a similar increasing trend as the temperature increased. The value of the benzene solubles increased from 80% at 285°C to 93% at 335°C. Therefore, increasing operating temperature helps to increase the oil yield and its solubles in benzene. However, if the operating temperature was too high, e.g., 350°C, and the retention time was long (120 min), there was solid char formed. The benzene solubles decreased to 89.1% as the operating temperature increased to 350°C. One explanation is that once the oil product was formed, it underwent an overoxidation and was further broken down thermally into smaller molecules until it became char. Some of the char were suspended in the post-processed water and categorized as part of the solid product which led to the drop of the oil yield. The char contained in the oil product would not dissolve in the solvent, thus contributed to the low benzene solubles.

On the other hand, the overall content of carbon and hydrogen in the oil did not change much as the temperature increased from 285°C to 350°C (fig. 2). As the operating temperature increased from 285°C to 305°C, the carbon content was approximately constant at about 70%. As temperature increased from 305°C to 350°C, the carbon content gradually increased from 70% to 78%. However, the hydrogen content decreased gradually as the temperature increased. The hydrogen content remained fairly constant at about 9.5% from 285°C to 305°C and decreased from 9.5% to 9.1% as the operating temperature increased to 350°C. As the results, H:C molar ratio dropped from 1.63:1 to 1.46:1. This is an 11.6% relative difference. High operating temperature has the potential to both enhance the oil yield by converting more organic matter into oil and improve oil quality by eliminating oxygen element in the oil product through more active combination of CO and oxygen element. Meanwhile, the elimination of oxygen element from oil product yielded less oil product (by weight). The compromise between the two outcomes led to the fluctuation

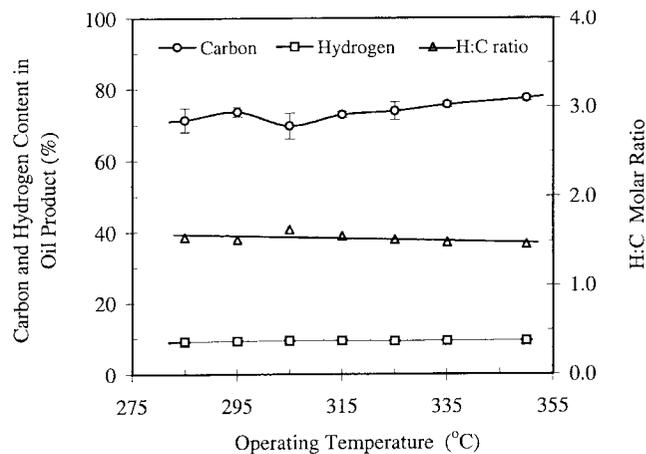


Figure 2—Temperature effect on the carbon and hydrogen contents. The operating conditions were CO:VS = 0.07 (wt) or p_{ini} = 690 kPa, RT = 120 min, TS = 20%, and feedstock pH = 6.1. The corresponding operating pressures were 7–18 MPa.

of the oil product yield through the temperature range and the constant increase of the benzene solubles.

Post-processed water is a major output of the TCC process. As most of the organic matter was converted into oil product, there was a small amount of the water-soluble organic matter remaining in the post-processed water. The water-soluble organic and other reductive minerals such as Fe^{2+} , Mn^{2+} , Mn^{4+} , and Cd^{2+} contribute to the COD of the post-processed water. Figure 3 shows the operating temperature effect on the COD reduction efficiencies of the TCC process. The COD reduction efficiency increased from 62% to 71% as the temperature increased from 275°C to 295°C. However, the COD reduction efficiencies were at about the same level of 70% at temperatures above 295°C. This reflects the same trend as the oil production efficiency for a similar reason. The high temperature promotes the reactive combination of CO with organic compounds and eliminates the oxygen element. Meanwhile, the CO also reduces the oxidative inorganic compounds to their

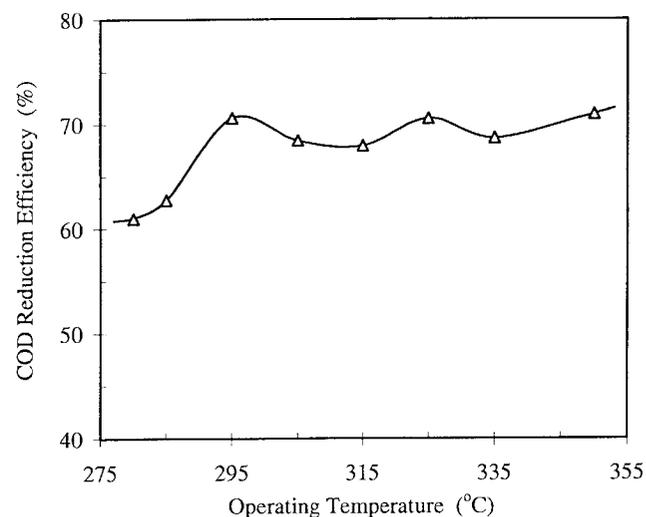


Figure 3—Temperature effect on COD reduction efficiency. The operating conditions were CO:VS = 0.07 (wt) or p_{ini} = 690 kPa, RT = 120 min, and feedstock pH = 6.1. The corresponding operating pressures were 7–18 MPa.

reductive states, which contribute to the increase of COD in the post-processed water. The measurements of some post-processed water samples showed that the carbon content of the post-processed water at operating temperature of 285°C was about 4.2%. This includes both organic carbon and inorganic carbon. This amount of carbon in the post-processed water is equivalent to a maximum possible COD of 112 000 mg/L if all were oxidized into CO₂. Some carbon such as the carbonate was, however, already in its highest oxidative state, thus does not contribute to the COD. The COD measurements of the post-processed water showed that the CODs were from 60 000 mg/L to 100 000 mg/L when the operating temperatures were from 275°C to 350°C. These COD measurements agree with the results of carbon analysis mentioned above, considering also that the carbonate does not contribute to the COD.

RETENTION TIME EFFECT

Retention time (RT) in this study was defined as the period of time maintained at the pre-set operating temperature. Retention time is a kinetic parameter and it affects the organic matter conversion rate and product distribution. Insufficient RT will lead to an incomplete conversion process. Excessive RT will result in overoxidization of the products and char formation. Figures 4, 5, and 6 show the experimental results of RT effect on the oil yields, solubles in benzene, and COD reduction efficiency, respectively. Each data point in the plots represents an average of two or three replications. The RT had a strong relationship with the oil product yield at 285°C (fig. 4). As the RT increased from 30 to 120 min, the oil yield increased from 12% to 57%, based on the initial VS input. This indicates that the depolymerization occurred gradually at 285°C. Extending RT increased the completeness of the organic conversion process, thus increasing the oil yield. However, the relationship between the RT and oil yield at 295°C and 305°C was not as strong as that at 285°C. The oil yields reached to 60% or higher in

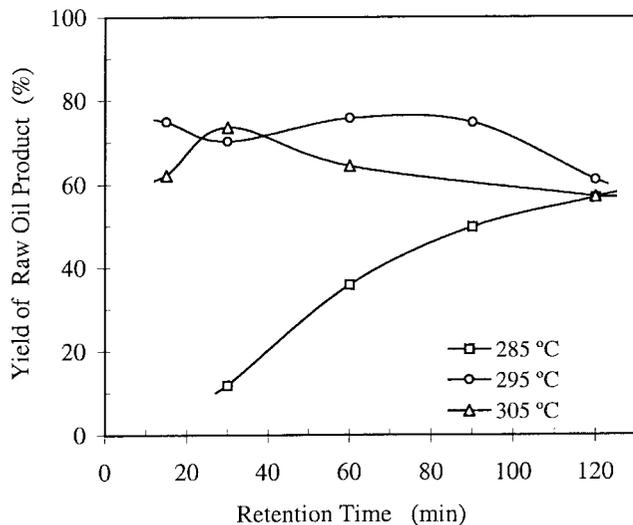


Figure 4—Effect of retention time on oil product yield at three operating temperatures. The operating conditions were CO: VS = 0.07 (wt) or p_{ini} = 690 kPa, TS = 20%, and feedstock pH = 6.1. The corresponding operating pressures were 7.6, 9.1, and 10.2 MPa, respectively.

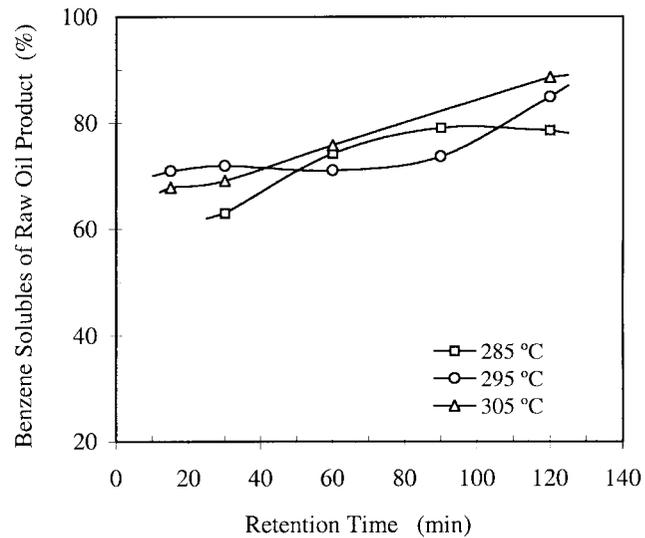


Figure 5—Retention time effect on the benzene solubles of the oil product at three different temperatures. The operating conditions were CO:VS = 0.07 (wt) or p_{ini} = 690 kPa, TS = 20%, and feedstock pH = 6.1. The corresponding operating pressures were 7.6, 9.1, and 10.2 MPa, respectively.

20 min when the temperatures were 295°C or 305°C. Unlike at 285°C, the oil yields decreased as the RT extended to 120 min. It is necessary to point out that the oil yields at 295°C were always higher than those at 305°C throughout the RT range, except at RT = 30 min. This phenomenon may be explained by the oil product quality versus its yield. At 305°C, the oil product contained less oxygen content and relative higher carbon content. When the carbon conversion rate was about the same as at lower temperatures, the total amount of oil product decreased which resulted in lower oil yields (fig. 4).

Figure 5 shows the relationship between RT and the benzene solubles of the oil product at three different operating temperatures. As RT increased from 30 to

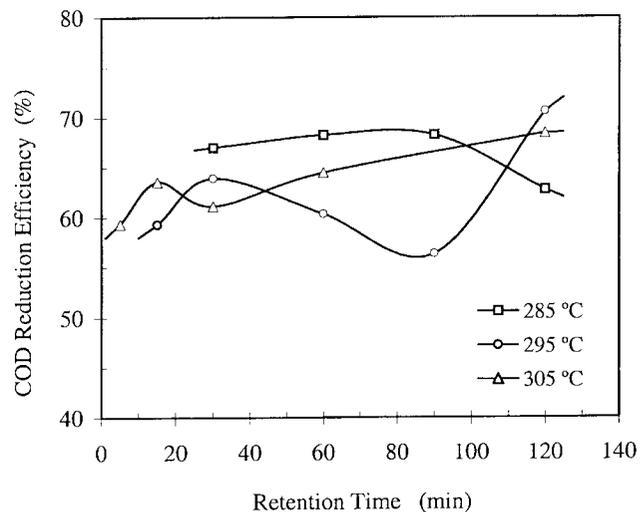


Figure 6—Retention time effect on COD reduction efficiency at three operating temperatures. The operating conditions were CO: VS = 0.07 (wt) or p_{ini} = 690 kPa, TS = 20%, and feedstock pH = 6.1. The corresponding operating pressures were 7.6, 9.1, and 10.2 MPa, respectively.

90 min, the benzene solubles at 285°C increased from 63% to 79% and leveled off thereafter. Compared to those at 285°C, the benzene solubles at 295°C showed higher values of about 70% at RT less than 30 min, but lower at RT 60 ~ 90 min. It increased to 85% as RT reached 120 min. The benzene solubles at 305°C were lower than those at 295°C when RT was 30 min or less. It was the highest when RT was longer than 60 min, increasing from 75% to 88%. The better oil quality, indicated by high solubles in benzene solvent, was offset by lower oil yields (see fig. 4).

The RT also affected the COD reduction efficiency as shown in figure 6. Overall, the COD reduction efficiency increased as the RT increased. However, the increasing rates were different at different operating temperatures. At 285°C, the COD reduction efficiency was virtually constant at 67% as the RT increased from 30 to 90 min. Then it decreased to 63% when RT increased to 120 min. Meanwhile, the COD reduction efficiencies increased 10% for those at 295°C and 305°C, from about 60% to 70%, although there was a COD reduction drop at RT 90 min when the temperature was 295°C. It is noticed that the COD reduction efficiencies at 285°C were higher than those at 295°C and 305°C when RT was 90 min or shorter. One possible explanation is that some of the water-soluble organic matter could not be completely oxidized due to highly active CO at 295°C and 305°C. There were also some reductive minerals and other inorganic compounds remaining in the post-processed water. These water-soluble and reductive compounds contributed to the high COD in post-processed water at high temperatures.

CONCLUSIONS

The operating temperature is key parameter for the TCC process in terms of oil product yields and benzene solubles. The operating temperature must be 285°C or higher to ensure oil formation. On the other hand, the operating temperatures higher than 335°C would lead to more solid char formation and thus reduce the oil yields. The necessary retention time for the process to convert organic matter to oil was dependent upon operating temperatures. The reaction rate increased and the retention time reduced at higher operating temperatures. At 285°C, the retention time of 120 min was necessary for the oil product yield to reach 60%, and the oil yield dropped significantly as the RT shortened. At 295°C and 305°C, it took less than 30 min to reach a 60% or higher yield. Increasing operating temperatures to 295°C and 305°C reduced the retention time to 30 min or less in order to achieve an oil product yield of 60% or higher. If the retention time was 60 min or longer at 295°C and 305°C, the oil yields started to decrease. The oil yields fell below 60% at retention time of 120 min. Meanwhile, increasing the retention time at temperature higher than 295°C did not increase COD reduction efficiencies because of the reductive atmosphere created by the high reactive CO. In conclusion, the proper operating temperature and retention time for the TCC process should be 295°C to 305°C and 15 to 30 min, respectively, based on the results of this study.

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