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The Gasification of Acetone via Partial Oxidation in Supercritical Water

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***Abstract*—**Organic solvents find various applications in many industrial sectors and laboratories as dilution solvents, dispersion solvents, cleaners and even lubricants. Millions of tons of spent organic solvents (SOS) are generated each year worldwide, prompting the need for more efficient, cleaner and safer methods for the treatment and resource recovery of SOS. As a result, acetone, selected as a model compound for SOS, was gasified in supercritical water to assess the feasibility of resource recovery of SOS by means of supercritical water processes. Experiments were conducted with an autoclave reactor. Gaseous product is mainly consists of H_2, CO, CO_2 and CH_4. The effects of three major operating parameters, the reaction temperature, from 673 to 773K, the dosage of oxidizing agent, from 0.3 to 0.5 stoichiometric oxygen, and the concentration of acetone in the feed, 0.1 and 0.2M, on the product gas composition, yield and heating value were evaluated with the water density fixed at about 0.188g/ml.

***Keywords*—**Acetone, gasification, SCW, supercritical water.

I. Introduction

WATER with both its temperature and pressure above its critical point is termed supercritical water (SCW). Like all other supercritical fluids, supercritical water, though being a gas, possesses both gaseous and liquid characteristics. The gaseous features include high diffusivity, compressibility and low viscosity, and the most prominent liquid-like feature is its high solubility. Furthermore, at supercritical state, water loses most or all of its hydrogen bonds and behaves more like a non-polar fluid, thereby allowing itself to dissolve and mix with organic matters into a single phase. This unique ability of SCW to form a single phase with organics is a great asset in many processes, in which the hindering mass-transfer and energy-transfer resistances are dramatically reduced. An outstanding feature of SCW is its extraordinarily high critical temperature, 647.4K, making SCW an excellent solvent for the reaction of organics, most of which are non-reactive at temperatures lower than the critical temperature of water. One more important property which makes SCW as a reaction medium particularly attractive is that SCW is absolutely environmentally safe. The density, viscosity, diffusivity, ion product of water as well as the solubility of metal salt in water all change dramatically near water's critical point. Therefore, controlling the solvent properties of water through adjusting the state of water is crucial in the applications of supercritical water. Since early 1980s, the unique characteristics of SCW have drawn much research efforts both in fundamentals and applications of SCW.

The application of SCW as a solvent to the reaction of organic matters can be categorized according to the amount of oxidizing agent used. If the amount of oxidizing agent added is more than that needed for complete oxidation, it is termed supercritical water oxidation (SCWO), applied mainly to the degradation of hazardous organic substances and to the treatment of wastewaters containing dilute hazardous organic substances. If insufficient amount of oxidizing agent for complete oxidation is added, it is a supercritical water partial oxidation (SCWPO), employed primarily in the resource recovery of organic wastes and in the gasification reactions. When no oxidizing agent is added, it is simply a thermal pyrolysis process taking place in the SCW environment.

Conventional gasification of organic matters produces not only product gases but also undesirable tars and chars, whose formation decreases the gas yield and hence lowers the gasification efficiency. A pioneering study [1] has shown that gasification of carbohydrates in SCW with ZrO_2 as the catalyst can produce solely gaseous products without tars or chars. The fundamental mechanism behind this marvelous discovery is not yet clear. It might be partially explained by the following reasoning. Firstly, undergoing gasification reactions in SCW environment, carbohydrates are closely surrounded by water molecules. This on one hand favors the hydrolysis of carbohydrates [2] which in turn may help to break carbohydrate polymers into smaller pieces or monomers, and on the other hand prevents the carbohydrates from dehydrating which is the main cause for the tarring or charring of carbohydrates. Secondly, water molecules could be the reactants of reforming reactions of the carbohydrates. The participation of water in the reactions favors the formation of lighter molecules, due to an increase in the hydrogen and oxygen content in the final products. Thirdly, SCW has high solubility of organic matters and is capable of forming a single phase with carbohydrates, thereby overcoming the limitation of heterogeneous heat and mass transfer. The technology of SCWPO not only combines the merits of thermal pyrolysis and oxidation of SCW, but also needs little or no external heat source by making use of the heat liberated from the partial oxidation to sustain the reactions. It is still at its infancy and a promising technology of the future.

In recent years, the potential of the SCWPO technology has been gaining recognition. It can apply not only to the treatment and resource recovery of organic wastes but also to the chemical reactions for the production of specific chemicals. The hydrogenation and desulfurization of dibenzothiophene via SCWPO was reported by Adschiri et al. [3]. Park et al. [4]

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attempted the transformation of waste tires into useful resources with SCWPO. Kim et al. [5] studied the partial oxidation of p-xylene in subcritical as well as supercritical water, and obtained high conversion percentage. Watanabe et al. [6], [7] investigated the degradation and partial oxidation of polyethylene and n-hexadecane in SCW. Richter and Vogel [8] tried to synthesize cyclohexanol and cyclohexanone from cyclohexane via SCWPO technology, and achieved high product selectivity. Sato et al. [9] tried to upgrade the value of asphalt through SCWPO. More recently, coking wastewater was treated using SCWPO by Wang et al. [10]. Ning et al. [11] gasified phenol by SCWPO and obtained quite positive results. The gasification of bitumen coal through SCWPO was attempted by Ge et al. [12] and Sato et al. [13].

In the present work, the SCWPO of acetone, selected as a model compound for SOS, was investigated experimentally to assess the feasibility of resource recovery of SOS by means of supercritical water processes. The effects of three major operating parameters, the reaction temperature, the dosage of oxidizing agent, and the concentration of acetone in the feed, on the product gas composition, yield and heating value were evaluated. Organic solvents find various applications in many industrial sectors and laboratories as dilution solvents, dispersion solvents, cleaners and even lubricants. Millions of tons of spent organic solvents (SOS) are generated each year worldwide, prompting a constant search for more efficient, cleaner and safer methods for the treatment and resource recovery of SOS. The current study helps to understand the feasibility of resource recovery of organic solvents by way of SCWPO technology.

II. Experimental Method

A. Materials

Reagent-grade acetone and hydrogen peroxide aqueous solution, 30 wt.% H_2O_2(aq), were employed as the organic reactant and the oxidizing agent, respectively. De-ionized water was used as the water source for SCW.

B. Apparatus and Procedures

A series of experimental runs was conducted with a batch-type autoclave reactor of 16-ml. The top of the autoclave is connected to a main valve, which in turn connects the product collection and separation unit. The autoclave, tubing and valves are all made of cold-worked 316L stainless steel rated 140 MPa at room temperature. The reactor system was estimated to withstand pressure up to 42 MPa at 773K, the highest operating temperature employed in this study. A typical experimental run begins by estimating the amount of reactants (including organics, de-ionized water and oxidizing agent) needed according to the target operating temperature and pressure; then, put the precisely weighed reactants into the autoclave, which is then carefully tightened to the required torque and placed in the furnace. Set the target temperature on the furnace and start heating until the target temperature is reached (in about 30 minutes). Meanwhile, temperature is recorded at a fixed interval of time. The reaction is allowed to continue for 60 minutes at the preset temperature to ensure the completion of the reaction. Then, the furnace is turned off, and the reactor system is removed from the furnace and cooled by forced air to room temperature in about 30 minutes. At this point, the pressure inside the reactor has reduced to a few atmospheric pressures. The main valve is carefully and slowly opened and the gaseous product is collected and weighed with its volume measured by water displacement method. The reactor is opened afterwards. The liquid product is collected and weighed, and the formation of solids is only qualitatively observed. Comparing the amount of the liquid product with that of the total amount of feed gives the amount of conversion of the reactant into gaseous product, and serves as an indicator to whether a leakage exists during an experimental run.

Our experimental design did not incorporate a thermocouple for direct monitoring of the internal temperature of the reactor, because previous experimental observations showed that the installation of a thermocouple into the bottom end of the reactor significantly worsens the temperature non-uniformity within the reactor. The temperature disparity with an internal thermocouple installed can be as high as 50 K. Direct temperature observation was made around the reactor with the thermocouple of the furnace. The internal pressure of the reactor was not directly measured with a pressure gauge, either, since no pressure measuring instruments are available which would not significantly interrupt the reactor system. Considering the ranges of temperature and pressure involved, the only viable pressure measurement instruments currently available are Bourdon-type gauges. However, a Bourdon tube, with an internal volume as high as 5ml, when connected to the reactor, becomes an external cooling zone for the reactor, since it must be located outside the furnace, resulting in the uncertainty of the effective reaction zone as well as of the effective reaction temperature. Alternatively, the internal pressure of the reactor is theoretically estimated. The molar percentage of water molecules in the SCW reaction environment mostly exceeds 95%, so ideal solution model applies to the water molecules and more than 95% of the total pressure is contributed by the water molecules. In the current study, the reaction pressure will be characterized by the apparent pressure, P_{AP}, which is defined as the thermodynamic equilibrium pressure exerted by water in the autoclave reactor containing only water, whose amount is identical to that of total water in the feed at the beginning of an experimental run. From the known amount of water and the volume of the reactor, the apparent pressure at various temperatures can be easily obtained from a steam table. In the SCW reaction environment, water molecules not only serve as the reaction solvent but also participate in the reactions to some extent. However the amount of water affected by the reactions is minor in comparison with the total amount of water present in the SCW system, estimated to be less than 1% of the total amount of water. Therefore, the discrepancy between the apparent pressure of water and the real reaction pressure should be no more than 5%. For instance, when the apparent pressure of water is 30 MPa, the real reaction pressure shall lie in the range of 30±1.5 MPa.

Open Science Index, Chemical and Molecular Engineering Vol:8, No:4, 2014 publications.waset.org/9997974/pdf

Gaseous product is weighed and analyzed for its hydrocarbons as well as H_2, N_2, O_2, CO and CO_2 contents with a GC-TCD (ThermoQuest TRACE 2000). The composition of hydrocarbons with five carbons or less is analyzed individually, and the composition for those with more than five carbons is lumped together. Condensates, i.e. the liquid products, are simply weighed. The presence of solid residues in the product is qualitatively observed and recorded.

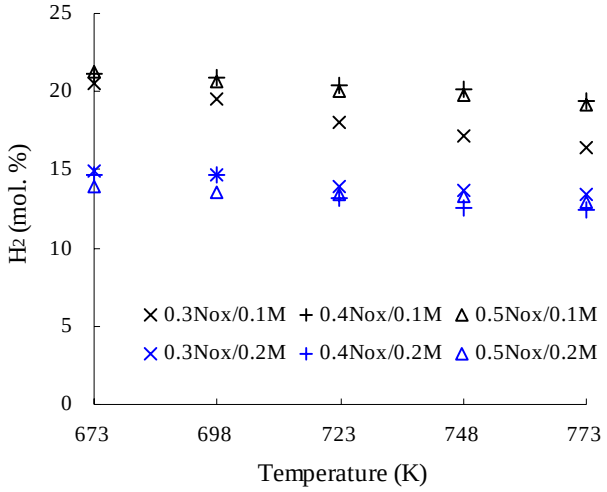


Fig. 1 H_2 concentration in product gas

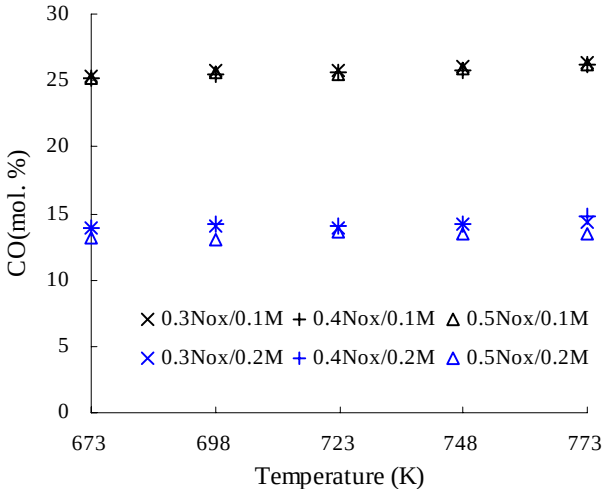


Fig. 2 CO concentration in product gas

Since direct monitoring was made on the furnace temperature instead of the internal temperature of the reactor, a number of pre-experiments were carried out to understand the dynamic relationship between the two temperatures. Put a fixed amount of water into the reactor and lock a thermocouple into the only exit port of the reactor, which is then placed in the furnace for heating. The internal temperature of the reactor and the furnace temperature were observed against the heating time. The internal temperature of the reactor significantly lags the furnace temperature, which takes about 10 minutes to reach the set point while the former needs approximately 30 minutes. Consequently, a total heating time of 90 minutes was employed for each experimental run to ensure a reaction time of more than 60 minutes.

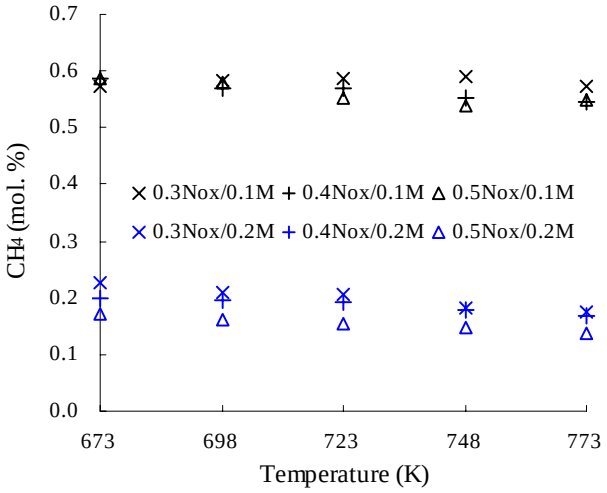


Fig. 3 CH_4 concentration in product gas

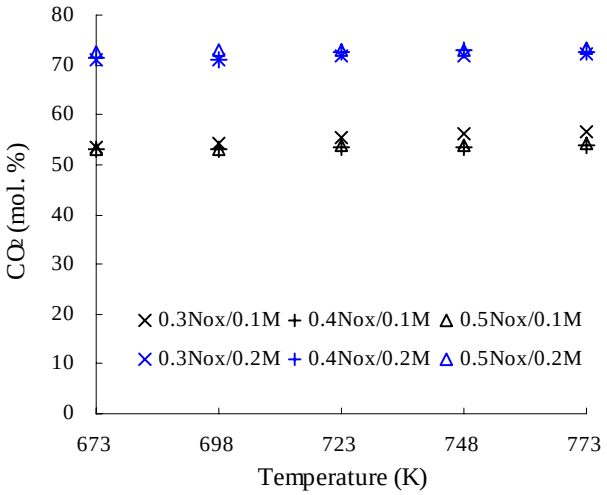


Fig. 4 CO_2 concentration in product gas

III. Results and Discussion

Three operating parameters investigated are reaction temperature, from 673 to 773K with an interval of 25K, concentration of acetone in the feed, 0.1 and 0.2M, and dosage of the oxidizing agent, 0.3, 0.4 and 0.5 stoichiometric oxygen, N_{ox}. One stoichiometric oxygen is defined as the amount of oxidizing agent necessary to completely oxidize the organic reactants, quite similar to concept of chemical oxygen demand for the water treatment. Therefore, 30 distinct experimental settings are possible. With two runs for each setting, a total of 60 experimental runs were completed. Water density was fixed at around 0.188g/ml in all experimental runs by using identical amount of total water, including the added water and the water in the hydrogen peroxide aqueous solution used as the oxidizing agent. The apparent pressure, P_{AP}, can be estimated based on the known water density and reaction temperature. It is approximately 26, 30, 34, 37 and 41 MPa for 673, 698, 723, 748 and 773K, respectively. Note that apparent pressure

Open Science Index, Chemical and Molecular Engineering Vol:8, No:4, 2014 publications.waset.org/9997974/pdf

appears to be linear with the reaction temperature for the range of temperature employed in this study.

The gaseous product from the SCWPO was found to consist mainly of CO_2, H_2, CO and CH_4 in decreasing order. The gaseous hydrocarbons of two to five carbon atoms were found to be negligibly scarce in the product gas, and hence were unaccounted for. Oxygen was normally not detected in the product gas, indicating that oxygen was depleted by the vigorous reactions in SCWPO. The liquid product, consisting of water, water soluble, and organic condensates, was collected, weighed and visually inspected. It usually looked clear and transparent when first collected and slowly turned into light-brownish color in a few hours. Its color often got darker with time in the first couple of days. Solid residues were generally not present in the product.

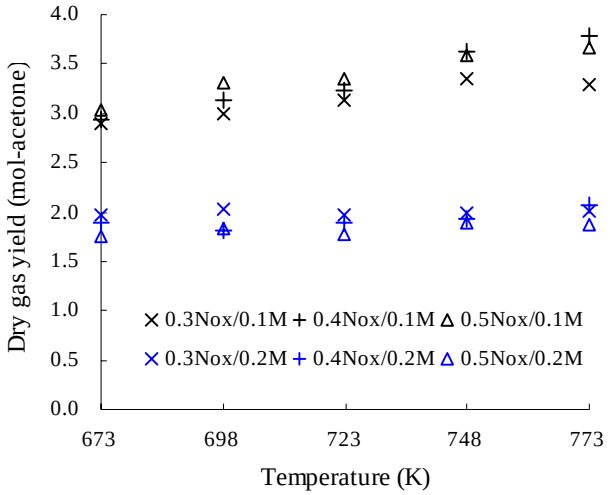


Fig. 5 Dry gas yield per mole of acetone

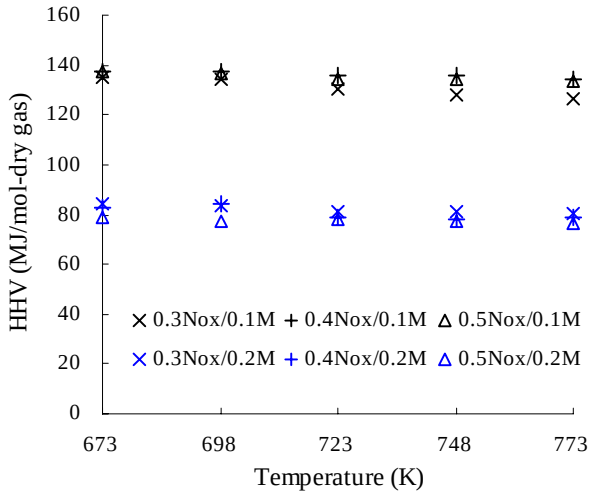


Fig. 6 HHV of dry product gas

The molar percentages of the main gas components, CO_2, H_2, CO and CH_4, are plotted in Figs. 1 through 4, respectively, against reaction temperature, with dosage of oxidizing agent and concentration of organic reactant as the parameters. As seen from Fig. 1, the concentration of hydrogen gas generally decreases gradually with rising temperature in the temperature range investigated. The influence of the dosage of oxidizing agent was found to be insignificant, except for the case of changing from 0.3 to 0.4 N_{ox} at 0.1M. To our surprise, the dosage of oxidizing agent has only a minimal effect on the SCWPO of acetone, not only shown in Fig. 1 but also in the remaining figures. Actually, a much larger effect was expected from it and further studies are needed to verify this observation. The most influential parameter in this study turned out to be the level of acetone concentration in the feed. The hydrogen content of the product gas is significantly lower in higher concentration of acetone in all corresponding conditions. This observation confirms a major drawback with the SCW gasification process previously reported in the literature [1], that organic matters, such as biomass, can be completely gasified in SCW if its concentration is low, e.g. lower than 0.1M. This is a major obstacle needed be overcome if the application of SCW to the gasification of organic materials will ever become practical.

The variation of the molar concentration of CO is shown in Fig. 2. Again, the operation temperature has only a slim effect. However, its effect on the CO concentration is opposite to that of hydrogen gas concentration. The CO concentration increases very slowly with temperature, while the hydrogen gas concentration decreases with temperature. This seemingly complimentary behavior of hydrogen gas and CO were also noted in the gasification of other organic maters [14]. As mentioned above, the dosage of oxidizing agent had little effect and the biggest effect resulted from the level of organic reactant concentration in the feed.

Figs. 3 and 4 display the variation of the methane and CO_2 concentrations in the product gas against reaction temperature, respectively. Methane concentrations observed are generally lower than one percent, while CO_2 has the highest concentration, from 50% to as high as 75%. The main operating parameters have similar effects on methane and CO_2 concentrations as on other gaseous components. That the dosage of oxidizing agent has virtually no effect on the concentration of CO_2 in the product gas was really unexpected. It was expected that with the increase supply of oxidizing agent in the feed, increased extent of oxidation should have significantly increased the CO_2 concentration. Hence, further study is needed to verify this unexpectancy.

The dry gas yield, number of moles of dry product gas produced per mole of acetone in the feed, and higher heating value (HHV) of the dry product gas are also exhibited in Figs. 5 and 6, respectively, versus major operating parameters. The dry gas yield and HHV were found to vary moderately with increasing temperature, especially in the case of low organic reactant concentration in the feed, marginally affected by the dosage of oxidizing agent, and marked influenced by the organic reactant concentration in the feed. The HHV of the dry product gas is low compared to common fuel gases such as natural gas due to the dilution effect of the high level of CO_2 in the gas.

Since apparent pressure is approximately linear with the reaction temperature for the range of temperature employed in

this study, results plotted against the apparent pressure are similar to those plotted against reaction temperature, presented in Figs. 1 through 6.

IV. Conclusion

The SCWPO of acetone was studied experimentally to investigate the effects of three major operating parameters, the reaction temperature, from 673 to 773K, the dosage of oxidizing agent, from 0.3 to 0.5 stoichiometric oxygen, and the concentration of acetone in the feed, 0.1 and 0.2M, on the product gas composition, yield and heating value while the water density was fixed at about 0.188 g/ml. It was found that the reaction temperature in the temperature range investigated had only moderate effect, the dosage of oxidizing agent had little effect, and the level of acetone concentration had enormous effect on the process. The observation of the SCWPO of acetone being barely affected the dosage of oxidizing agent was unexpected and needs verification by further studies.

Acknowledgments

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References

[1] M. Watanabe, H. Inomata and K. Arai, "Catalytic hydrogen generation from biomass (glucose and cellulose) with ZrO2 in supercritical water," *Biomass and Bioenergy*, vol. 22, no. 5, pp. 405-410, 2002.
[2] M. Sasaki, B. Kabyemela, R. Malaluan, S. Hirose, N. Takeda, T. Adschiri and K. Arai, "Cellulose hydrolysis in subcritical and supercritical water," *J. of Supercritical Fluids*, vol. 13, no. 1-3, pp. 261-268, 1998.
[3] T. Adschiri, R. Shibata, T. Sato, M. Watanabe and K. Arai, "Catalytic Hydrodesulfurization of Dibenzothiophene through Partial Oxidation and a Water-gas Shift Reaction in Supercritical Water," *I&EC Research*, vol. 37, no. 7, pp. 2634-2638, 1998.
[4] Y. Park, J. T. Reaves, C. W. Curtis and C. B. Roberts, "Conversion of Tire Waste using Subcritical and Supercritical Water Oxidation," *Journal of Elastomers and Plastics*, vol. 31, no. 2, pp. 162-179, 1999.
[5] Y. L. Kim, S. J. Chung, J. D. Kim, J. S. Lim, Y. W. Lee and S. C. Yi, "Uncatalyzed Partial Oxidation of P-xylene in Sub- and Supercritical Water," *Reaction Kinetics and Catalysis Letters*, vol. 77, no. 1, pp. 35-42, 2002.
[6] M. Watanabe, T. Adschiri and K. Arai, "Polyethylene Decomposition via Pyrolysis and Partial Oxidation in Supercritical Water," *Kobunshi Ronbunshu*, vol. 58, no. 12, pp. 631-641, 2001.
[7] M. Watanabe, H. Inomata, M. Osada, T. Sato, T. Adschiri and K. Arai, "Catalytic Effects of NaOH and ZrO2 for Partial Oxidative Gasification of n-Hexadecane and Lignin in Supercritical Water," *Fuel*, vol. 82, no. 5, pp. 545-552, 2003.
[8] T. Richter and H. Vogel, "The partial oxidation of cyclohexane in supercritical water," *Chemical Engineering and Technology*, vol. 25, no. 3, pp. 265-268, 2003.
[9] T. Sato, T. Adschiri, K. Arai, G. L. Rempel and F. T. Ng, "Upgrading of Asphalt With and Without Partial Oxidation in Supercritical Water, *Fuel*, vol. 82, no. 10, pp. 1231-1239, 2003.
[10] Y. Z. Wang, S. Z. Wang, Y. Guo, Y. M. Gong,; X. Y. Tang and J. Zhang, "Partial oxidative gasification of coking wastewater in supercritical water," *Advanced Materials Research*, vol. 788, pp. 409-412, 2013.
[11] Z. Y. Ning, Q. Q. Guan, N. Ping and J. J. Gu, "Partial oxidation of phenol in supercritical water," *Advanced Materials Research*, vol. 726, pp. 2714-2717, 2013.
[12] Z. Ge, S. Guo, L. Guo, C. Cao, X. Su, H. Jin, "Hydrogen production by non-catalytic partial oxidation of coal in supercritical water: Explore the way to complete gasification of lignite and bituminous coal," *International Journal of Hydrogen Energy*, vol. 38, no. 29, pp. 12786-12794, 2013.
[13] T. Sato, P. H. Trung, T. Tomita, N. Itoh, "Effect of water density and air pressure on partial oxidation of bitumen in supercritical water," *Fuel*, vol. 95, pp. 347-351, 2012.
[14] M. T. Liang, S. M. Chern, M. Y. Yu, S. C. King and S. Y. Lin, "Gasification of Oil and Sewage Sludges in Subcritical and Supercritical Water," in *Proc. 8th Meeting on Supercritical Fluids*, Bordeaux, 2002.

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