On The Development of a Counter-Flow Mixing Reactor for Fast Hydrothermal Liquefaction

Arturs Curakovs, Khanh-Quang Tran*.

Department of energy and process engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway.
khanh-quang.tran@ntnu.no

A laboratory-scale continuous tubular flow reactor system has been developed for fast HTL (hydrothermal liquefaction) of lignin, adopting the nozzle reactor concept with a counter-flow mixing design. The reactor is capable of very fast heating and tolerating solid particles suspended in the liquid stream flowing through the reactor. The system has been tested for fast HTL of lignin residues from steam explosion, which was prepared and continuously pumped into the reactor in the form of a slurry solution of 25 wt. % lignin (125 μm in size) in water and 2 wt. % of cooking oil as emulsifier. This paper presents and analyses the development, the emulsification study, and the first test of the nozzle reactor design for fast HTL of lignin.

1. Introduction

Fast hydrothermal liquefaction (Fast HTL) involves fast processing of biomass in hot compressed water (below 374°C, 22.1 MPa) for production of HTL oil or bio-crude. Similar to fast pyrolysis, the process of fast HTL requires higher heating rates, aiming at maximized bio-crude yields and minimized coke formation. It is because HTL is represented by both beneficial primary reactions (pyrolytic & hydrolytic degradation) and non-beneficial secondary reactions (recombination and secondary cracking) (Brand et al. 2014). In the case of slow heating, biomass undergoes step-by-step hydrolytic degradation, pyrolytic degradation, as well as recombination and secondary cracking reactions if elevated temperatures are applied. Under fast heating conditions, hydrolytic and pyrolytic cleavage would be taking place simultaneously. Dominance of either pathway, hydrolytic or pyrolytic cleavage, depends on the final reaction temperature. If higher final temperatures are applied, a long residence time would be favour of the non-beneficial secondary reactions of recombination and secondary cracking. Therefore, HTL oil yield can be maximized by fast heating combined with short reaction time. In addition to this, fast heating also has positive effects on product characteristics, including the fuel properties and functional groups of HTL oil (Brand et al. 2014, Bach et al. 2016). These effects are similar to that of catalyst addition to HTL process (Bach et al. 2016). This fact may beyond the state-of-the-art HTL technology with respect to the conversion efficiency, product selectivity and thus end-use compatibility.

The concept of fast HTL has been validated (Bach et al. 2014, Bach et al. 2016). The method of improving the conversion efficiency and product selectivity for HTL by fast heating has been successfully demonstrated (Bach et al. 2014, Bach et al. 2016). A key issue for making the concept of fast HTL sustainable for production of liquid biofuel and chemicals from solid biomass is to develop a continuous flow tubular reactor, which can 1) achieve fast heating; 2) tolerate solid biomass particles suspended in a water stream flowing through the reactor; and 3) be up-scalable (Tran 2016).

Recently, it has been identified that the concept of nozzle reactor may be suitable for fast HTL of biomass at both laboratory and industrial scales (Tran et al. 2017). This work reported results from a preliminary (computational fluid dynamics) study on developing a CFD model for the nozzle reactor design suitable for fast HTL. The results indicate that the mass flowrate ratio of hot and cold flows plays the most important role in establishing high heating rates in the reactor. Tests of the model for pure water (viscosity = 0.001 Pa.s) with a mass flowrate ratio of 60:20 (hot/cold, mil/min) gave very good mixing and thus high heating rate. Effect of the total mass flow on the temperature profile in the reactor was not significant.

More recently, a system reaction including a nozzle reactor has been developed in our Thermal Lab of the Department of Energy and Process Engineering at Norwegian University of Science and Technology (NTNU), constructed, and characterized with respect to temperature profile for 1) pure water flows; 2) a cold flow of water containing 10% w/w of glucose as model compound. The characterization results are in agreement with those from the CFD prediction, with reasonable differences due to the adiabatic assumption of the CFD model. Difficulties in feeding the reaction system with thicker slurry solutions of solid biomass in water have been encountered. These difficulties are associated with the quick settling of solid biomass particles in water. Therefore, efforts have been made to overcome these difficulties, focusing on size reduction of biomass particles and use of emulsifier. This paper reports results from the emulsification study followed by a quick test of the developed reaction system for fast HTL of lignin as solid biomass.

2. Material and experimental method

2.1 Nozzle reactor design and construction

Figure 1 presents schematically the nozzle reactor design and reaction system, which has been succesfully developed for production of nanoparticles from equaeous solutions of metal salts (Lester et al. 2006, Sierra-Pallares et al. 2016). For fast HTL application, certain modifications are needed, such as replacement of the aqueous metal salt stream in Figure 1A and Figgure 1B with a lignin slurry stream.

(A) Schematic of a nozzle reactor
(Lester et al. 2006)

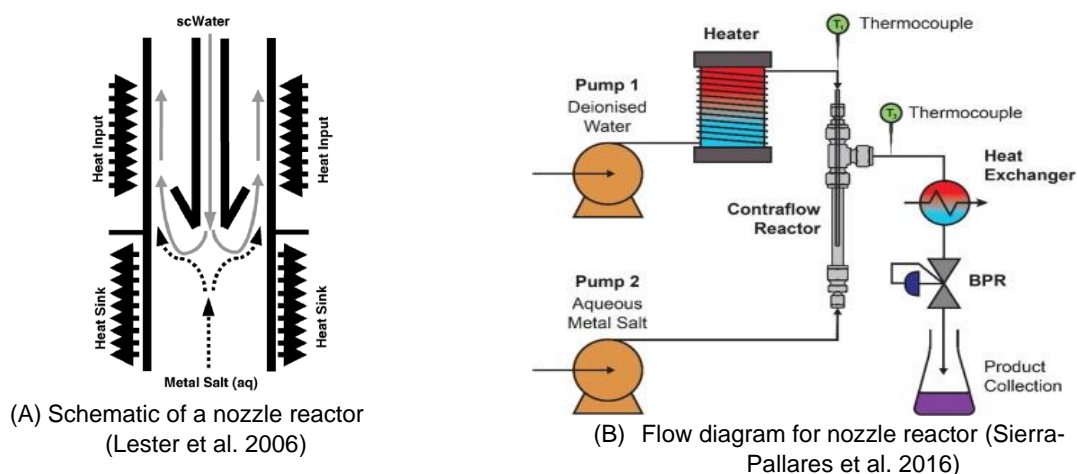(B) Flow diagram for nozzle reactor (Sierra-Pallares et al. 2016)

Figure 1: Schematic diagram of the nozzle reactor and continuous flow reaction system developed for hydrothermal synthesis of nanoparticles (Lester et al. 2006, Sierra-Pallares et al. 2016)

Essentially, the reactor in Figure 1 is a pipe-in-pipe concentric setup in which the internal pipe has an open-ended nozzle with a cone attached (optional). The optional cone would help intensify the mixing at the nozzle exit, in the same manner as a thin film reactor, spinning disc or spinning cone reactors (Boodhoo et al. 2001, Brechtelsbauer et al. 2001, Yatmaz et al. 2001). The "hot" stream (or flow) of preheated water is fed downwards through the internal pipe, reaching out at the nozzle exit inside the external pipe. The "cold" stream is fed upwards through the external pipe. The reactor outlet is located on top of the external pipe, leading the reactant mixture to a heat exchanger (Figure 1B) for cooling, with good potentials for heat recovery if and when needed. Because of the impingement of the hot and cold streams at the nozzle exit, the forced counter-current mixing process is enhanced by the natural convection due to the density difference between the two steams. As a result, very good mixing and thus high heating rates can be established in the reactor. In addition, it has been reported that nozzle reactors developed for hydrothermal synthesis of nanoparticles were free from the blockage problem, even at a pilot scale of much higher concentrations of metal salt precursor than the laboratory scale (Gruar et al. 2013).

2.2 Experimental setup for fast HTL

Figure 2 schematically presents the lab-scale continuous flow reaction system including a nozzle reactor developed at the Department of Energy and Process Engineering, Norwegian University of Science and Technology (NTNU) for fast HTL of biomass. The heart of the reaction system is a *nozzle reactor* located in the middle. The *Tubular Furnace* is employed to preheat water by means of a double-coil unit capable of producing

two separate streams of hot water. One of these streams (*the hot stream*) is fed into the reactor by *Pump 1* to heat up the cold stream upon impinging and mixing of the two streams at the nozzle exit. The other is for external heating of the reactor, compensating the heat loss to the surrounding. The high pressure and high viscosity *Syringe Pump* (TELEDYNE ISCO 60-5364-229 Modell 500 HV) is used for feeding biomass slurry to the reactor. The system pressure is controlled by the *Back Pressure Regulator* (BPR) connected directly to *Vessel 1*. In addition to Vessel 1, which acts as a flash tank for gas-liquid separation, *Vessel 2* is introduced into the system to make it possible for continuous operation of the system with respect to product removal at high pressures. The initial pressure required to boot the BPR at start is provided by the nitrogen gas cylinder directly connected to *Vessel 2*.
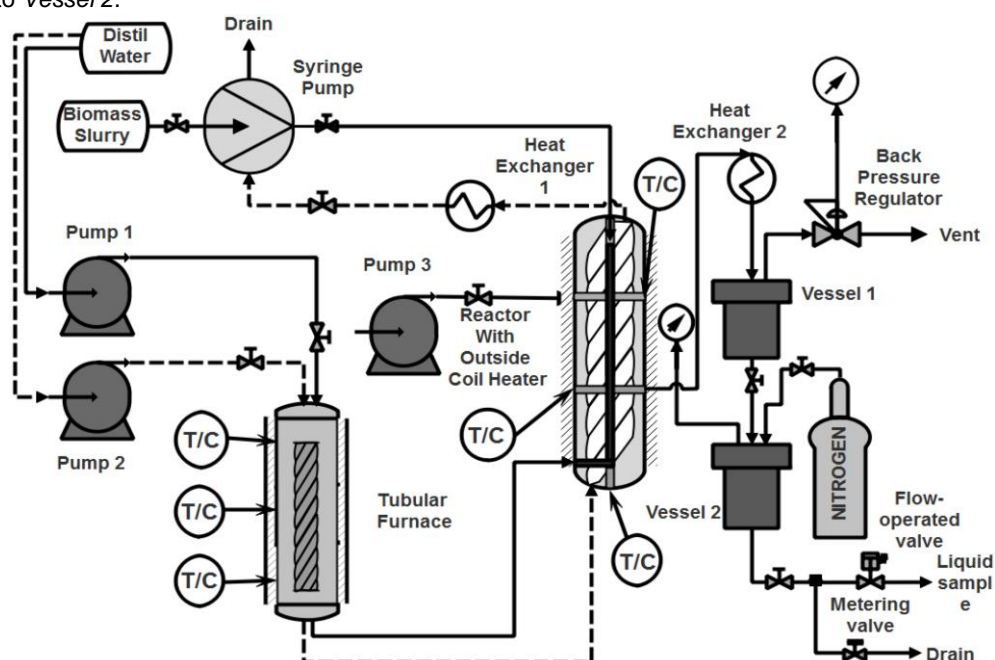

Figure 2: Schematic diagram of the fast HTL reaction system developed at NTNU

2.3 Biomass sample and emulsification method

Solid lignin residue from steam explosion for 2nd generation bioethanol production was obtained from Sekab AB in Örnsköldsvik, Sweden, and used as feedstock for the present study. The lignin powder sample was dried in a muffle furnace at 105°C for 24 hours and then milled to reduce the particle size. Lignin powders with a particles size smaller than 125 μm were obtained for an emulsification study. A low-cost vegetable cooking oil from Rema1000 and pyrolysis oil was tested as emulsifier. Since the mass ratio of emulsifier over lignin should be as small as possible, the emulsifiers were dissolved in methanol before mixing with lignin powders in a mortar. The mixture of lignin powders soaked with emulsifier in methanol was then dried and milled again before preparing emulsion or slurry solutions of 20 wt % of lignin with emulsifier in water. The study was carried out using 50 mL scaled transparent polypropylene tubes, which allowed visual inspection and measurement of the settling time and segregation between the liquid (water) and solid (lignin particles) within two hours.

3. Results and discussion

3.1 Emulsification study and pumping test

Figure 3 presents the effect of addition 2.5 wt % of cooking or pyrolysis oil as emulsifier on the settling time and distance of slurry solutions containing 20 wt. % lignin in water. The addition of both pyrolysis oil and cooking oil as emulsifier appears to have positive effects on the settling time, which is inversely proportional to the settling distance. However, cooking oil exhibited better results in slowing down the settling velocity. Therefore, cooking oil was selected for further studies, including the investigation of effect of the added amount of cooking oil emulsifier and lignin particle size on the settling time, from which the results are presented in Figure 4 and Figure 5, respectively. It is interesting to see that the settling time increases with increasing amount of emulsifier added to linin (Figure 4) or with increasing lignin concentration (Figure 5).
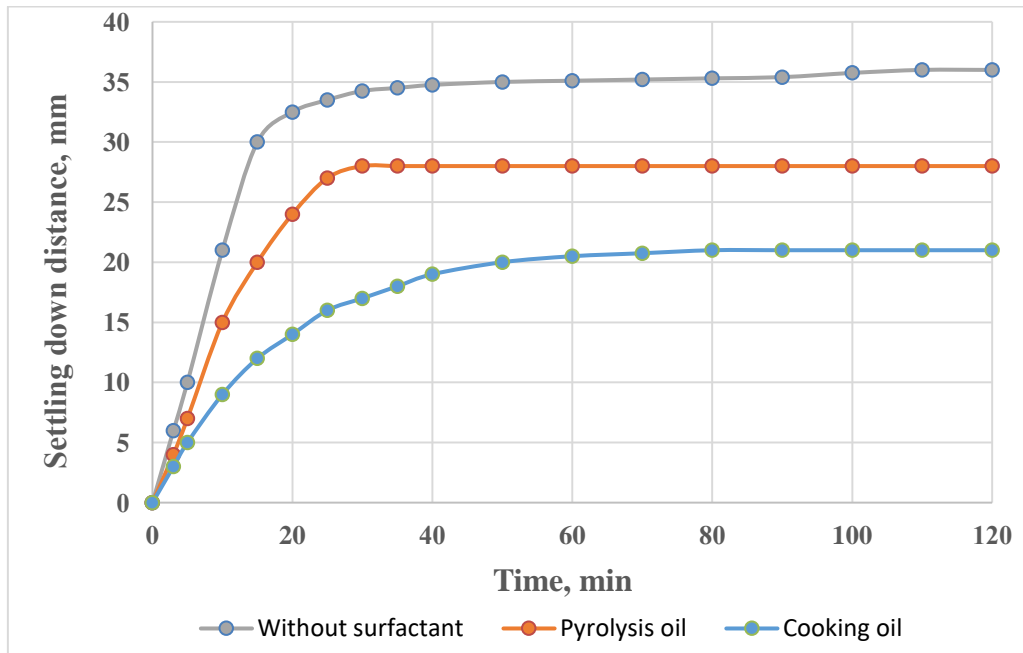
Figure 3: Effect of emulsifier type on settling time (20 wt. % of lignin with 2.5 wt. % emulsifier of 125 µm size in water)

Along with the settling study, various pumping tests of the slurry solutions prepared from the lignin with different particle sizes and contents, impregnated with different amounts of cooking oil emulsifier were performed on the *Syringe Pump* (TELEDYNE ISCO 60-5364-229 Modell 500 HV). It is interesting to observe that there were two extreme situations when it was not possible to pump the slurry solutions. The first one was when the settling time was too short because the too small content of emulsifier used. The second and opposite extreme occurred when the concentration of emulsifier was so high that a creaming process was observed and it was not possible to fill up the pump with the slurry solutions. The best result for the performance tests of the pump was obtained for the slurry solution of 25 wt. % lignin, 2 wt. % cooking oil emulsifier and lignin particle size 125 µm.
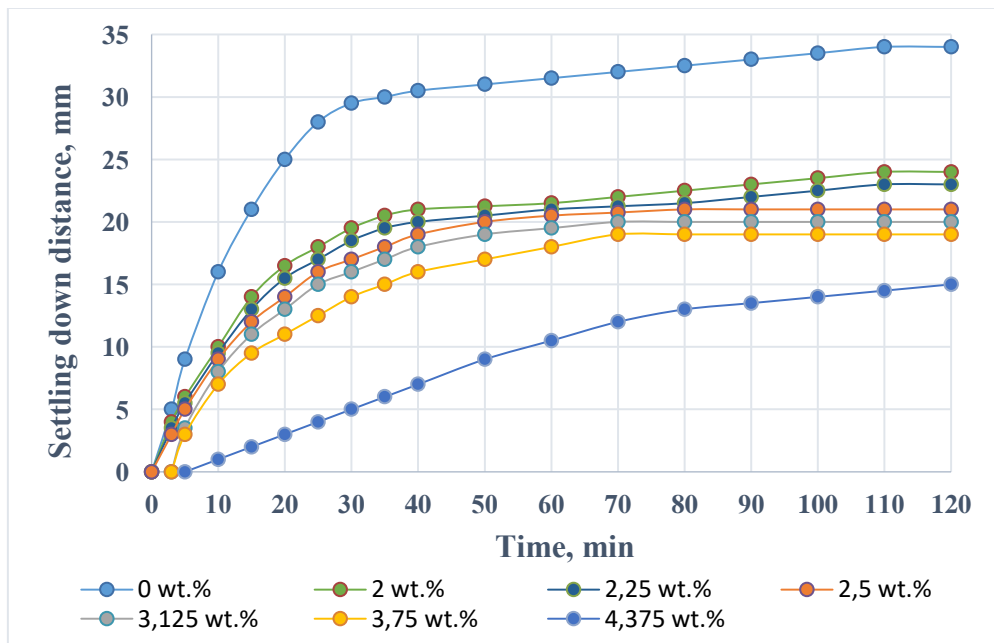

Figure 4: Effect of cooking oil addition on settling time (20 wt. % of lignin of 125 µm size in water)
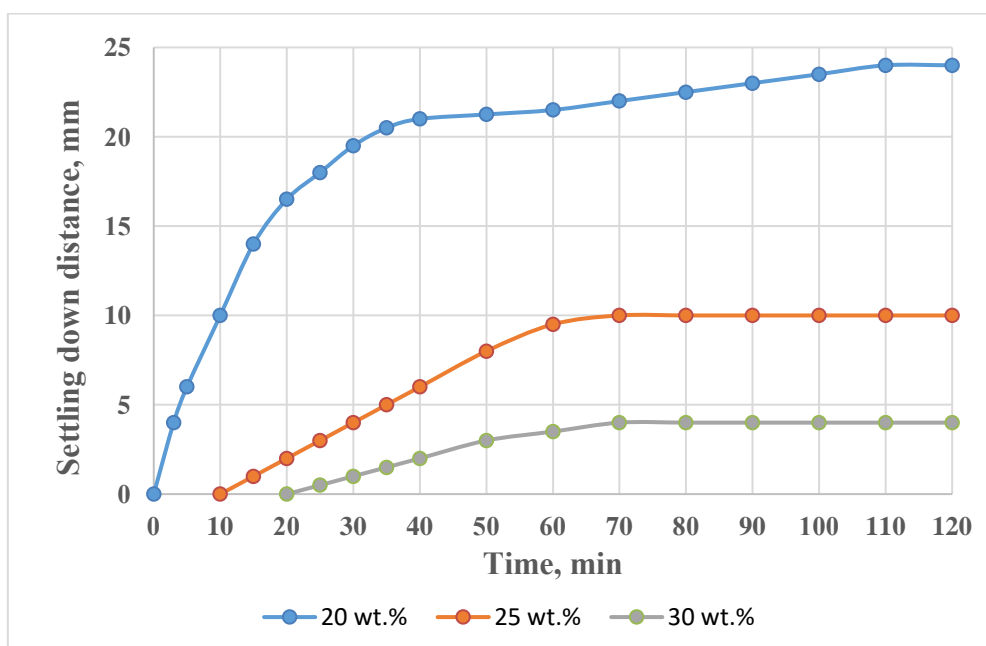
Figure 5: Effect of lignin content on settling time (lignin of 125 µm size in water, cooking oil emulsifier of 2.5 wt. %)

3.2 First test of the nozzle reactor system for fast HTL of lignin

The best result for the performance tests of the slurry solution of 25 wt. % lignin, 2 wt. % cooking oil emulsifier and lignin particle size 125 µm was adopted for the first test of the reaction system shown in Figure 2 and Figure 6A. Under the conditions of 40 ml/min as the total volumetric flow rate through the reactor, 1/3 as the ratio of cold stream over hot stream, and 350°C as the reaction temperature, the reaction system was continuously and successfully operated for 20 minutes with an estimated oil yield within 40-50 wt. % on a dry basis. The HTL oil product was collected and shown in Figure 6B (in dichloromethane) and Figure 6C (after having been vacuum dried).
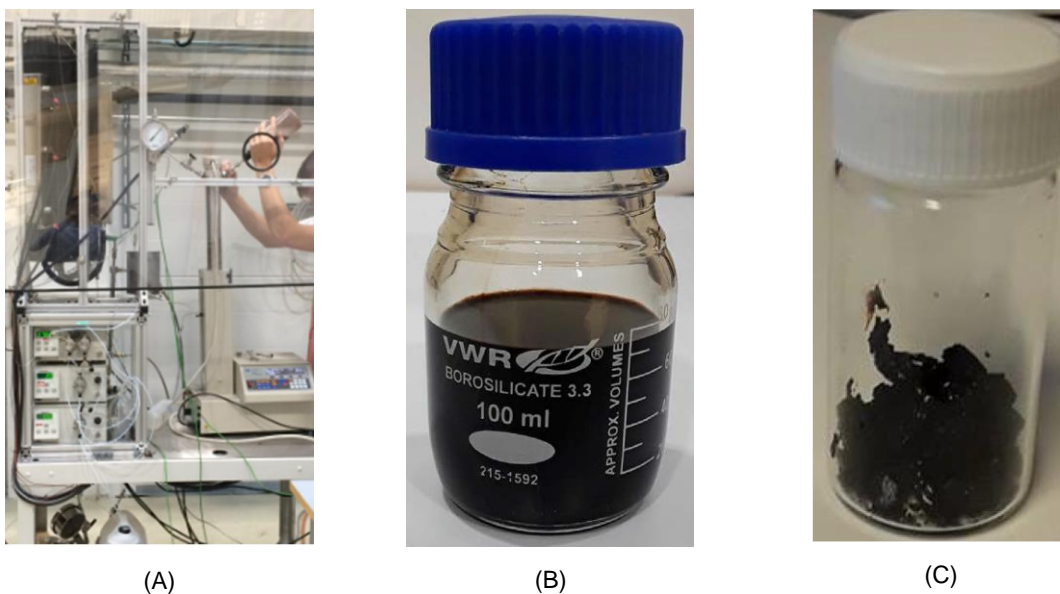

(A)　　　　　　　　　　(B)　　　　　　　　　　(C)

Figure 6. (A) Lab view of the fast HTL reaction system at NTNU; (B) HTL oil in dichloromethane before rotational evaporation; and (C) HTL oil produced via fast HTL of lignin.

It is important to note that, continuous operations longer than 20 minutes for the system was not possible due to the limited volume (500 ml) of the high viscosity syringe pump. In addition, it was not able to achieve more precise mass balance calculation due to the practical limitations of the system in establishing the steady state within the limited time of the continuous pumping capacity. Two identical pumps in parallel, equipped with a stirring mechanism, are needed for fully continuous operations of the reaction system and further study.

4. Conclusions

The concept of nozzle reactor design has been identified to be suitable for realizing continuous fast HTL of solid biomass, producing higher quality HTL oil. The reactor is capable of very fast heating and tolerating solid particles suspended in the liquid stream flowing through the reactor. A laboratory-scale setup has been developed, adopting the nozzle reactor concept, with modifications suitable for fast HTL. The system has been successfully tested for fast HTL of lignin residues from steam explosion, which was prepared and continuously pumped into the reactor in the form of a slurry solution of 25 wt. % lignin (125 μm in size) in water and 2 wt. % of cooking oil as emulsifier. The results from the first test of the nozzle reactor design for fast HTL of lignin is promising. However, further investigations and optimizations of the reactor geometry and the process are needed.

Acknowledgement

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