REACTOR SYSTEM DEVELOPMENT TO REDUCE COAL LIQUEFACTION SEVERITY

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Keywords: Loop Reactors, Coal Liquefaction, Hydrogenation

INTRODUCTION

The hydrogenation of aromatic hydrocarbons is of interest not only because of the commercial interest of the reaction, but also because the liquefaction of coal and the subsequent product upgrading involves the hydrogenation of aromatic rings [1]. A number of reactions of industrial importance, such as the hydrogenation of various organic compounds and the hydrodesulfurization of petroleum fractions, involve reactions between two fluids in the presence of a solid catalyst. Coal liquefaction is one such reaction in which coal slurried in a solvent reacts with hydrogen to yield liquid products. The goal in a coal liquefaction process is to convert coal into a clean liquid fuel by increasing the hydrogen content of coal derived liquids and removal of heteroatoms such as sulfur, nitrogen and oxygen.

The efforts to improve yield and selectivity from coal liquefaction have focussed on the development of improved catalysts [2-4] and the use of different hydrogen donors [5-7]. These attempts have met with limited success due to the autocatalytic nature of the free radical propagation. The hydrogen supply rates are not sufficient to saturate the free radicals generated at longer residence times used in conventional reactors such as tubing bomb microreactors and stirred autoclaves. The development of new and improved reactor systems with better reaction control and improved mass transfer rates will reduce some of the problems associated with coal liquefaction.

REACTOR DESIGN CONCEPT

Coal liquefaction reactions proceed via a free radical propagation mechanism. The free radical propagation increases exponentially and very high gas-liquid mass transfer rates are necessary to saturate the free radicals and prevent retrogressive reactions. Commercial gas-liquid contactors are not capable of providing sufficiently high gas-liquid mass transfer rates to prevent hydrogen starvation and thus retrogressive reactions from occurring. An alternative approach to increase the yield and improve the product selectivity in free radical type reactions is to control the rate of free radical propagation so that only practically achievable mass transfer rates would be required. The reactor system used in this study is based on this alternative approach.

The approach used in developing the reactor system was two-fold: 1) a reactant flow pattern was developed which would allow versatility in reaction rate controllability and 2) a gas-liquid contactor design was sought that would provide the highest mass transfer rates per unit volume. The higher the mass transfer rate can be made per unit reactor volume via gas-liquid contactor design, the farther the operational range of the reactor system over which the rate of retrogressive reactions would be low.

A bang-bang control strategy was used to regulate the reaction rate. A cyclic switching from high to low reaction temperatures was used to control the free radical propagation rate. The adjustable control parameter selected was the frequency of the cyclic switching of the reaction temperature. Physically, this was accomplished using a recycle loop type reactor in which the temperature in part of the loop was kept high (reaction zone) and that in the remainder of the loop it was lower (quenching zone). The frequency of cyclic switching of the reactant temperature could be varied simply by changing the reactant recycle flow rate. The mass transfer requirements per reaction cycle could be maintained within a range that could be satisfied by practical gas-liquid contactors, simply by optimizing the recycle flow rate. This type of reactor flow arrangement is similar to jet loop type reactors, which have been employed when reaction rates are very high and the reactions are mass transfer limited.

REACTOR SYSTEM

The conventional slurry reactor designs are modified in industrial reactors to achieve specific objectives such as higher heat and mass transfer capabilities, higher catalyst efficiency, better reactor performance and selectivity, etc [8]. The high heat and mass transfer rates, easy control over the degree of backmixing, and simple design have made loop reactors very attractive for both industrial and academic purposes. A jet loop type reactor was designed and used in this study.

Jet loop reactors with hydrodynamic jet flow drive are suitable for gas-liquid-solid processes which require rapid and uniform mass distribution and high mass transfer rates. The reactor system developed for this study operates in a semi-batch mode with the gas being supplied continuously. The liquid and the solid constituting the slurry are recycled through the reactor system.

The reactor system employs stainless steel columns measuring eight inches in length and one inch in outer diameter (O.D.) as reactors. The reactors were connected with 0.5 inch O.D. tubing and were placed in a fluidized sand bath for efficient temperature control. The reactor tubes were filled with stainless packing rings, as heat transfer in a packed column with metal rings is highly efficient due to a large surface area per unit volume of liquid. The slurry was recycled through the closed loop reactor system by a pump. The slurry passes through a preheater before entering the reactor system. The slurry is heated to the desired temperature in the preheater by using ethylene glycol as the heating fluid. The glycol was heated in a cylindrical tank fitted with three electric heaters. A centrifugal pump was used to circulate the ethylene glycol between the preheater and the tank. The slurry passes through the preheater into the reactor tubes and through the reactors into a chiller. The slurry is cooled in the chiller using tap water as the coolant. A gas-liquid decoupling chamber separates the gas and the liquid coming out of the chiller. The liquid flows into the suction side of the pump to be recycled. The gas flows into a gas recirculation unit. The unit consists of three gas-liquid separators and an air driven gas compressor. The gas is drawn from the decoupling chamber into the separators in succession. The gas is fed to the compressor and pumped into the slurry along with fresh gas at the gas-liquid contactor on the discharge side of the pump. Any vapors in the gas condense in the separators and are drained after the run.

The reactant gas is fed into the reactor system through a gas-liquid contactor before the slurry enters the preheater. A number of gas-liquid contacting devices are available to increase the gas-liquid mass transfer rates. These include motionless mixers, column packings, high shearing mechanical agitators and different kinds of nozzles. An improvement in the gas-liquid mass transfer will result in stabilization of free radicals and could result in improved product selectivity.

Different types of nozzles are being used increasingly to enhance mass transfer during gas-liquid contacting. Two phase nozzles, where both the phases come into contact inside the nozzle, were used in this study due to their high mass transfer capabilities and their ease of use in a closed system. A very efficient type of two phase nozzle employed in the present study is the slot injector introduced by Zlokarnik [9]. In a slot injector, the mixing chamber which is circular becomes slot shaped gradually keeping the cross-sectional area constant. The slot shape results in a lower pressure drop, because the shear rate increases along the convergent surface. This produces a fine gas dispersion with the free jet retaining a large portion of its kinetic energy. In addition, the free jet leaves as a flat band and mixes rapidly with the surrounding liquid, reducing bubble coalescence. The reactor system is shown in Figure 1.

EXPERIMENTAL

Naphthalene hydrogenation experiments in the reactor system were conducted using tetralin as the solvent. A predetermined quantity of naphthalene and catalyst (5% Pd on carbon) was mixed with the solvent in a beaker. The mixture was sonicated for about ten minutes to effectively disperse the catalyst. The slurry was charged into the reactor system when the desired reaction temperature was reached (130-160°C). The system pressure was then increased to 125 psig by feeding in hydrogen. The pressure was monitored and the system was charged back to 125 psig after a 10 psig drop. A sample was withdrawn for analysis approximately a minute after gas recharging. The reaction was allowed to proceed until no drop in pressure was observed. The system was then drained and the product mixture was filtered before sampling for analysis. The system was flushed with toluene or tetralin after every run.

RESULTS AND DISCUSSION

The model reaction used in the present study to evaluate the reactor system was the hydrogenation of naphthalene. This is a very important reaction during the liquefaction of coal to regenerate the hydrogen donor solvent (tetralin). The catalyst used in the study was a commercial 5% Pd on carbon. Palladium is the most active hydrogenation catalyst, but is strongly inhibited by the presence of sulfur compounds [10]. However, the use of palladium in model compound studies (without the presence of sulfur) will facilitate evaluation of new and improved reactor systems under conditions which are not severe. This helps to reduce the "bugs" in the reactor system and, in addition, will also demonstrate improvements in conversion and selectivity.

The results of naphthalene hydrogenation in the present reactor system and in tubing bomb microreactors (TBMR) are shown in Tables 1 & 2. It appears from the tubing bomb results that the catalyst is deactivated very rapidly when the temperature is

increased from 120°C to 135°C, resulting in no conversion. The catalyst requirement in the tubing bomb was very high (35% based on naphthalene) at 120°C to obtain 93% conversion. There was no conversion in the TBMR at 165°C with 10% catalyst loading, but when the tubing bomb experiments were conducted with repeated heating and cooling every three minutes, 86% conversion was obtained in 7.5 minutes. The repeated heating and cooling is similar to the conditions in the reactor system, where the reactants are exposed to the high temperature for a very short time (6-10 seconds). The naphthalene conversion in the reactor system was nearly complete (Table 1) under similar conditions with much lower catalyst loading and less time. In the TBMR, the reactants are exposed to high temperature throughout the reaction time resulting in an exponential increase of free radicals. The mass transfer rates are not adequate to saturate all the radicals and this leads to polymerization of free radicals resulting in the deactivation of the catalyst. In the reactor system however, the reactants are subjected to high temperature for a very short time per pass, reducing the probability of free radical polymerization.

The effect of catalyst loading on naphthalene hydrogenation in the reactor system (Table 1) was used to determine if gas-liquid mass transfer was controlling the reaction. A plot of reciprocal reaction rate vs reciprocal catalyst loading indicated that gas-liquid resistance is about 25% of the total resistance at the lowest catalyst loading and about 50% at the highest loading, indicating that the reactor is operating in a regime where gas-liquid mass transfer is only partially controlling. The mass transfer coefficient K_{la} determined from the experimental results was 6.0/min.

A limitation of the reactor system for use with severe reaction conditions was the performance of the mechanical pump. The pump was not capable of handling slurries under these conditions and suitable custom made pumps were prohibitively expensive. To overcome this limitation, a gas driven pumping system was developed and integrated to the reactor system. The reactor system with the gas-driven pumping system has been used for naphthalene hydrogenation under elevated pressures (800-1000 psig). Attempts are being made at present to use the system for coal liquefaction.

CONCLUSIONS

A loop reactor system has been developed for use with reaction systems such as coal liquefaction that are gas-liquid mass transfer limited. The reactor system has the ability to process slurries and permits better control of free radical generation/reaction and provides higher mass transfer rates than conventional reactors. The reactor system was tested using naphthalene hydrogenation as a model reaction and performed much better than the conventional tubing bomb microreactors. The amount of catalyst required was considerably less than that required in the microreactors. A unique gas-driven pumping system was developed and integrated to the system because of the prohibitive cost of a suitable mechanical pump that could withstand coal liquefaction conditions. The reactor system will be used to coprocess coal with waste oil. Improvements in coal conversion/selectivity will be compared with those obtained in conventional reactors.

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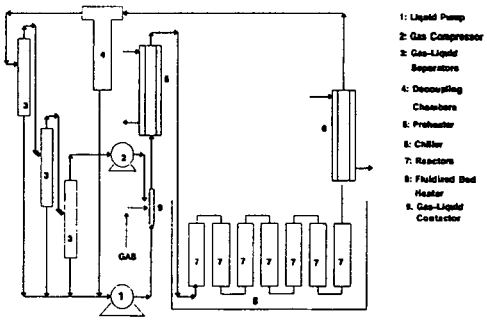

Figure 1. Jet Loop Reactor System

Table 1. Naphthalene hydrogenation (Reactor system)			
Catalyst (5.0%)*		Catalyst (7.5%)*	
Time (min)	Conversion (%)	Time (min)	Conversion (%)
7.0	17.07	3.5	24.75
9.0	31.20	6.5	33.13
14.0	47.22	9.0	45.14
20.0	64.30	10.75	54.50
27.0	85.44	15.0	69.62
37.0	98.81	20.50	88.88
		30.0	99.21
Catalyst (10.0%)*		Catalyst (15.0%)*	
Time (min)	Conversion (%)	Time (min)	Conversion (%)
4.0	35.34	3.5	39.92
6.5	40.18	5.0	44.55
8.75	54.14	7.25	63.94
11.25	70.82	9.50	78.89
14.50	86.57	15.0	99.14
19.00	98.41		

* wt% based on the amount of naphthalene used
Tetralin: 750 ml
Naphthalene : 129.9 gm (18% of Tetralin)
Average reactor inlet Temperature: 123°C;
Average reactor outlet Temperature: 153°C;
Pressure: 120 psig

Table 2. Naphthalene Hydrogenation (Tubing bomb reactor)			
10% Naphthalene*, 10% Catalyst**			
Temperature (°C)	Pressure (psig)	Time (min)	Conversion (%)
90	150	30	0
105	300	60	20
120	300	60	36
126	300	60	0
18% Naphthalene*, 10% Catalyst**			
Temperature (°C)	Pressure (psig)	Time (min)	Conversion (%)
90	150	30	0
165	150	30	0
165	300	30	0
10% Naphthalene*, 35% Catalyst**			
Temperature (°C)	Pressure (psig)	Time (min)	Conversion (%)
120	300	30	93
18% Naphthalene*, 14.57% Catalyst**, Cooling frequency 3 min			
Temperature (°C)	Pressure (psig)	Time (min)	Conversion (%)
165	100	3.0	38.26
165	100	6.0	73.85
165	100	7.5	86.09

* Wt% based on the amount of tetralin used
** Wt% based on the amount of naphthalene used