

## CHAPTER II

### LITERATURE REVIEW

TS-1 catalyzed processes are advantageous from the environmental point of view as the oxidant is aqueous  $\text{H}_2\text{O}_2$ , which turns into water, and the reactions, operated in liquid phase under mild conditions, show very high selectivities and yields reducing problems and cost of by-product treatment. TS-1 can catalyze a variety of useful oxidation reactions and the hydroxylation of benzene by  $\text{H}_2\text{O}_2$  to phenol in the presence of TS-1 is also well known. Many researches have been written about the development of preparations of TS-1 and conditions for this reaction but no one has studied about the new alternative of the contacting technique that forces a reaction system to proceed under transient condition.

This chapter divides the reviewed works into two parts, i.e., (a) the TS-1 catalyst and the hydroxylation of benzene by  $\text{H}_2\text{O}_2$  over the TS-1, (b) the periodic operation in various reactions. An attempt will also be made to summarise the present knowledge and understanding of various factors influencing the conversion of the hydroxylation of benzene reaction under periodic operation. In the last section of this review, comments on previous studies that have directly influenced the aims of this study are given.

#### 2.1 Literature reviews

##### 2.1.1 The TS-1 catalyst and the hydroxylation of benzene by $\text{H}_2\text{O}_2$ over the TS-1

Kraushaar-Czarnetzki and van Hooff (1989) reported that TS-1 could also be obtained from [Al]ZSM-5 by dealumination and subsequent treatment with titanium tetrachloride. The obtained TS-1 exhibited the same catalytic properties as hydrothermally synthesized TS-1 of high purity. Moreover, their experimental result showed that the selectivity of their catalyst was strongly affected by the presence of small amounts of non-framework titania.

Thangaraj *et al.* (1990) studied the hydroxylation of benzene with  $\text{H}_2\text{O}_2$  over various zeolites. They found that benzene remained unreacted over silicalite-1,  $\text{TiO}_2$  (both amorphous and crystalline), and also in the absence of catalysts. The selectivity for the conversion of  $\text{H}_2\text{O}_2$  to hydroxy benzenes decreased in the order  $\text{TS-1} > \text{Fe-TS-1} > \text{Al-TS-1} > \text{Fe-ZSM-5} > \text{Al-ZSM-5}$ . The selectivity to phenol however, followed the reverse order. An interesting feature was that while phenol was the only product over pure acid zeolites (Fe-ZSM-5 and Al-ZSM-5), *p*-benzoquinone, the secondary product was formed in appreciable quantities over titanium-containing zeolites (TS-1, Fe-TS-1 and Al-TS-1). The selectivity for *p*-benzoquinone decreased in the order:  $\text{TS-1} > \text{Fe-TS-1} > \text{Al-TS-1}$ . The acid strength of these zeolites followed the reverse trend i.e.,  $\text{Al-TS-1} > \text{Fe-TS-1} > \text{TS-1}$ . Protonation of phenol over acid zeolites probably suppressed the further electrophilic reaction leading to dihydroxy benzenes.

TS-1 samples of different particle size were synthesized and investigated by van der Pol *et al.* (1992). Smaller particles were more active than larger particles. From calculation of the Weisz modulus it could be concluded that large zeolite particle were not fully utilized because of pore diffusion limitations. The product distribution was also influenced by particle size.

Martens *et al.* (1993) studied the hydroxylation of phenol with  $\text{H}_2\text{O}_2$  on EUROTS-1 catalyst. They reported that the calcination conditions of EUROTS-1 was critical. An increase of calcination temperature from 400 to 500 °C resulted in a substantial increase in activity. Static calcination generated less active catalysts, probably due to incomplete removal of template or its residues. The higher *ortho/para* ratio in the hydroxylated products observed on EUROTS-1 that was calcined under static conditions was used as an indication to show that the active sites in the interior of the crystals were partially blocked. In the presence of small amounts of solvent, a replacement of acetone by methanol resulted in an increase of the *p*-selectivity of EUROTS-1.

Weitkamp *et al.* (1997) investigated samples of TS-1 which had different mole ratio of Si/Ti. Samples prepared according to two different synthesis procedures could differ significantly in their hydrophobic/hydrophilic surface properties as revealed by the Modified Hydrophobicity Index. For Si/Ti ratio above ca. 40,



Modified Hydrophobicity Index decreased linearly with increasing titanium content which had been attributed to the increased formation of polar Si-O-Ti bridges in the zeolite framework. For TS-1 samples with higher titanium content, Modified Hydrophobicity Index strongly depended on the method of preparation and was considerably influenced by the formation of additional titanium-containing species in extra-framework positions. From the results of the catalytic characterization in the hydroxylation of phenol they could concluded that, in particular, TS-1 samples with high titanium content were the more active, the lower their Modified Hydrophobicity Index.

Bengoa *et al.* (1998) studied the influence of TS-1 structural properties and operation conditions on benzene catalytic oxidation with  $H_2O_2$ . They mentioned that small changes in the preparation conditions led to the presence of extra-framework titanium. In the benzene hydroxylation reaction using TS-1 prepared by the method of Thangaraj *et al.* (1990), the presence of sodium traces in the solid or  $CH_3OH$  in the reaction mixture changed the activity drastically. These results were attributed to a deactivation of active  $Ti^{4+}$  sites. In addition, the synthesis conditions might be controlled carefully to get pure TS-1, since the presence of extra-framework titanium inhibited benzene hydroxylation.

The use of environmentally detrimental organic solvent created problems in product separation and solvent recycle which were energy intensive steps. Hence, it was important to develop suitable methodology where the oxidation reactions catalyzed by TS-1 using  $H_2O_2$  as an oxidant could be carried out in the absence of organic solvents. In 1999, Kumar *et al.* tried to investigate the enhancement in the reaction rates in the hydroxylation of aromatics over TS-1/ $H_2O_2$  under solvent-free triphase conditions. They reported that the reaction rates of the hydroxylation of aromatics (such as benzene, toluene and anisole) were enhanced under triphase conditions (solid-liquid-liquid) compared to that obtained under biphasic conditions in the presence of a co-solvent (solid-liquid). While in the presence of a co-solvent (like acetone, acetonitrile or methanol) a long induction period was observed, in the solvent-free conditions the induction period was almost absent. In the case of substituted benzenes *para*-hydroxy product was predominantly obtained under the triphase conditions. However, in the biphasic condition the formation of *ortho*-isomer

was preferred. Probable factors responsible for an enhancement in the activity and a change in regio-selectivity were suggested to be: Relative hydrophobic nature and restricted pore dimensions of TS-1; Diffusive resistance faced by the substrate with an organic co-solvent in biphasic while such a resistance was minimized in triphase.

Li *et al.* (2001) reviewed the effect of titanium species in TS-1 prepared by hydrothermal method on the catalytic activity. They reported that the form of titanium atoms incorporated into the framework of TS-1 synthesized using tetrapropylammonium bromide as template differed from that using the classical method. But the symmetry of TS-1 changed from monoclinic to orthorhombic with the increase of titanium content in both methods. The  $\text{Ti-O}_2^-$  originated from framework titanium and  $\text{H}_2\text{O}_2$  had moderate stability and might be active site in oxidation reaction. TS-1 synthesized using tetrapropylammonium bromide as template did not contain anatase, but contained a kind of partly condensed titanium species with six-fold coordination. The titanium species might correspond to 270-280 nm band in UV-VIS spectra and also could form  $\text{Ti-O}_2^-$ . But, this kind of  $\text{Ti-O}_2^-$  was very stable and could not be catalytic active site. Therefore, the six-fold coordination titanium species might be inactive in both the oxidation reaction and the decomposition of  $\text{H}_2\text{O}_2$ . The hypothesis had been further proved by the phenomena that the titanium species was easily washed off using acid, and acid treating would not influence the catalytic performance of TS-1.

### 2.1.2 The periodic operation in various reactions

Periodic operation of catalytic processes have been investigated for many years. The literature up to almost the end of 1992 has been summarized in an excellent review by Silveston *et al.* (1995).



**Table 2.1** A list of reactions studied under periodic operation from 1968-1992 (Silveston *et al.*, 1995)

Authors	Year	Process	Forced parameter	Investigated effects
Lehr <i>et al.</i>	1968	EtOH dehydration to diethyl ether	Flow	Study of process nature
Denis and Kabel	1970	As above	Flow	Selectivity
Wandrey and Renken	1973	Hydrocarbons oxidation (propene, cyclohexene)	Concentration	Product distribution
Renken <i>et al.</i>	1974	EtOH dehydration to diethyl ether	Concentration	Selectivity
Helmrich <i>et al.</i>	1974	Ethylene hydrogenation	Concentration	Rate
Baiker and Richarz	1976	As above	Concentration	Rate
Renken <i>et al.</i>	1976	Ethylene oxidation	Concentration	Selectivity
Dautzenberg <i>et al.</i>	1977	Fischer-Tropsch synthesis	Concentration	Product distribution
Briggs <i>et al.</i>	1977-80	SO <sub>2</sub> oxidation	Concentration	Rate
Leupold and Renken	1977	Ethyl acetate from ethylene and acetic acid	Concentration	Rate
Al-Taie and Kershenbanm	1978	Butadiene hydrogenation	Concentration	Selectivity
Bilimoria and Bailey	1978	Acetylene hydrogenation	Concentration	Selectivity
Crone and Renken	1979	Styrene polymerization	Concentration	Rate, product distribution
Cutlip	1979	CO oxidation	Concentration	Rate
Abdul-Kareem <i>et al.</i>	1980	As above	Concentration	Rate
Lee <i>et al.</i>	1980	Saponification of diethyl adipate	Concentration	Selectivity
Silveston and Hudgins	1981	SO <sub>2</sub> oxidation	Concentration	Rate
Jain <i>et al.</i>	1982-83	NH <sub>3</sub> synthesis	Concentration	Rate
Wilson and Rinker	1982	NH <sub>3</sub> synthesis	Concentration	Rate
Adesina <i>et al.</i>	1984	Fischer-Tropsch synthesis	Concentration	Rate
El-Masry	1985	Claus reaction	Concentration	Rate
Nappi <i>et al.</i>	1985	Low-pressure methanol	Concentration	Rate
Müller-Erlwein and Guba	1988	Methacrolein from isobutyraldehyde	Concentration	Selectivity
Haure <i>et al.</i>	1989	SO <sub>2</sub> oxidation in trickle bed	Flow	Rate
Saleh-Alhamed <i>et al.</i>	1992	Propylene oxidation to acrolein	Concentration	Selectivity
Strots <i>et al.</i>	1992	SO <sub>2</sub> oxidation in CSTR	Concentration	Conversion

The performance of the Fischer-Tropsch synthesis (FTS) under forced cyclical changes in feed composition was reviewed by Adesina *et al.* (1995). Six catalysts had been investigated by two separate research teams. Most studied had employed a strategy using periodic exposure of the catalyst to pure H<sub>2</sub>. Experimental evidence was that H<sub>2</sub> pulsing provided a significant increase in the time average rate of formation of the lower carbon number paraffins for all the catalysts considered. Cobalt was the only catalyst for which olefin production also increased. Product distribution was also modified by H<sub>2</sub> pulsing, but the modification depended on the

catalyst. For Ru and Co catalysts, there was a decrease in the mean carbon number and a shift towards paraffinic products. The Mo catalysts investigated showed an increase in the mean carbon number under composition forcing, but at cycle periods that depressed rates of hydrocarbon formation. With Fe, CH<sub>4</sub> formation was strongly stimulated, but the product distribution of the other hydrocarbon products was unchanged. FTS mechanisms proposed in the recent literature seem adequate to explain qualitatively the composition forcing experiments.

Amariglio *et al.* (1995) mentioned that homologation of methane was thermodynamically disfavored. However, a two-step procedure using metal catalysts under non-oxidative conditions allowed the thermodynamic limitations to be circumvented. Metal catalysts, such as Pt, Co and Ru were exposed first to methane and then to hydrogen. They carried out these two steps at atmospheric pressure and at the moderate temperature. The chemisorption of methane was accompanied by the release of hydrogen whereas coupling of H-deficient CH<sub>x</sub> adspecies might take place. Numerous higher alkanes up to C<sub>7</sub>-C<sub>8</sub> were then removed by supplying hydrogen at ordinary pressure and at the same temperature as that of the first step. The driving force could be found in the energy which had to be supplied in order to compress part of the dilute hydrogen removed in the first step to make it usable in the second one.

Gulari *et al.* (1995) studied the periodic and transient operation of catalytic CO oxidation reactors. Based on experimental evidence, they concluded that periodic operation led to time-averaged rates of reaction higher than that possible under steady-state operation conditions for supported Pt and Pd catalysts in which there was strong inhibition of the rate by one of the reactants. Experimentally, strongly peaked responses in the reaction rate to step changes in concentration of reactants was indicative of a system in which rate enhancements might be possible through concentration cycling.

Hydrogenolysis for deprotection of amino acid was studied in a trickle bed reactor containing gas-liquid-liquid-solid four phases by Yamada and Goto (1997). When organic and aqueous solutions were continuously introduced into the four-phase reactor, the catalytic activity gradually decreased due to the deposit of phenylalanine (main product) on the surface of the catalyst. This problem could be



solved by periodic operation with flow of organic and aqueous solutions in the reaction period and with flow of only aqueous solution in the washing period. Although the catalytic activity gradually decreased in the reaction period, it could be completely regenerated by a washing period of 30 min using distilled water at a flow rate of  $1.7 \times 10^{-7} \text{ m}^3/\text{s}$ . The optimum conditions for periodic operation were investigated by simulation. They suggested that only organic solution should be allowed to flow in the reaction period instead of the mixture of two solutions to obtain higher concentrations of the main product.

The periodic operation of the selective NO reduction with propane over alumina was investigated by Aida and Kawakami (1997). Under steady operation, it was supposed that competitive consumption of the intermediate by  $\text{O}_2$  dominates. Under periodic operation, however, formation of the intermediate occurred during the absence of  $\text{O}_2$  in the gas phase. That was to say,  $\text{NO}_2$  was formed during the lean period (rich in  $\text{O}_2$ ) and it might be adsorbed on the alumina surface. The adsorbed  $\text{NO}_2$  reacted with hydrocarbon (HC) during the subsequent rich period (rich in HC). From the experiment, the effect of the period on the time-averaged NO conversion showed that the NO conversion decreased inversely to the period for period  $> 5 \text{ s}$ . It was considered that the adsorption amounts of  $\text{NO}_2$  and/or the intermediate in one cycle increased with extending the period up to 5s. For period  $> 5 \text{ s}$  the adsorption of  $\text{NO}_2$  might be saturated before the switching to  $\text{C}_3\text{H}_8$  or the intermediate might be used up before  $\text{O}_2$  injection so that the averaged conversion decreased.

Aida *et al.* (1999) studied the effect of diffusion and adsorption-desorption on periodic operation performance of NO-CO reaction over supported noble metal catalysts. The model calculations for the effect of intrapellet diffusion showed that it was significant on the performance under periodic operation even if it was not under steady state. Strong adsorption of a reactant enlarged the difference in the performance of the catalysts which had the active component at different radial locations. The location of active metals, such as platinum and rhodium in the different depth of the support pellet, improved the  $\text{NO}_x$  removal under periodic operation.

The cyclic operation of the oxidative dehydrogenation of propane over a V-Mg-O catalyst by the alternate feeding of propane and oxygen gas mixtures was investigated by Creaser *et al.* (1999). They reported that the response of the reaction products following a step-change in composition determined the cyclic conditions that resulted in an improved yield of propene. By alternating propane and oxygen with a 1:1 cycle split, time-average propene yields higher than steady state could be obtained. The optimal cycle period was found to be about 60 s. This 60 s period provided high propane conversion, as well as high propene selectivity. The cycle split could be varied by shortening the oxygen-feed half of the cycle with little effect on the time-average results. The oxygen half-cycle needed only to be long enough to reoxidize the catalyst. The propane feed scheme was varied by feeding increasing amounts of propane in the oxygen half-cycle. The change in feed scheme caused an increase in the time-average propane conversion that resulted in some further improvement in the propene yield despite some loss in propene selectivity.

Unsteady-state liquid flow modulation was investigated for hydrogenation of alpha-methylstyrene to cumene in a hexane solvent over 0.5% Pd on alumina spheres by Khadikar *et al.* (1999). Typically, a high liquid mass velocity and completely wetted catalyst were desirable for liquid-limited reactions, whereas a low liquid mass velocity and partially wetted catalyst were preferable in gas-limited reactions. Performance enhancement under gas-limited conditions was observed to be greater when gas supply is enhanced, i.e., at lower space time and lower cycle split. Maximum enhancement of about 60% was possible with a cycle split of 0.25 at the lowest liquid mass velocity under gas-limited conditions. Performance enhancement under liquid-limited conditions was observed only with Base-Peak flow modulation and seen to be possible only under poorly irrigated conditions (low mean liquid mass velocity) in the trickle bed. Performance enhancement was shown to be a strong function of the induced flow modulation frequency and indicative of the natural frequency of the governing process.

The trickle-bed reactor specifications and the operation conditions for the hydrogenation of  $\alpha$ -methylstyrene in a cumene solution using Pd/Al<sub>2</sub>O<sub>3</sub>-catalyst under periodic operation was studied by Lange *et al.* (1999). The result of the experimental



indicated that the increased and decreased catalyst wetting, the optimal influence of the mass transfer processes (gas-liquid, gas-solid, liquid-solid), the development of more channels (destruction of liquid pockets) in the catalyst bed were some of the causes of improved reactor performance. The simulation with an unsteady-state heterogeneous model demonstrated that the wetting efficiency had a very strong influence on the global reaction rate and on the conversion, respectively.

Stradiotto *et al.* (1999) studied the hydrogenation of crotonaldehyde under periodic flow interruption in a trickle bed. It appeared likely that at low liquid flows, steady-state reaction rates were lower than periodic ones because the catalyst was nonuniformly and only fractionally wetted. As a result, the gas reactant might be quite accessible to the catalyst, but without the second reactant presented on most of the surface, the net effect was a low rate of reaction. The importance of periodic addition of liquid reactant was to increase the efficiency of wetting, and, despite the probability of greater diffusion resistance from the liquid phase, to enhance the likelihood that the two reactant streams were in contact over a wide portion of the total catalyst surface, thereby increasing the overall rate of reaction. At high liquid flows, the steady-state operation was a good way to carry out reaction in a trickle-bed reactor when the two reactants were fed in separate streams. The fact that the apparent rate constant was now significantly higher than for low liquid flows suggested that an increased liquid flow rate enhanced the wetting efficiency and markedly increased the fraction of the catalyst surface on which reaction proceeds. Some poorly irrigated sections were likely present, possibly in the form of very thin liquid films, regions that allowed for good rates of diffusion of gas to the catalyst surface in addition to a high level of catalyst used.

Periodic operation of the Deacon process was studied by Nieken and Watzenberger (1999). They observed that there were some problems arising in two step Deacon process such as corrosion, space time yield, chlorine purity, catalyst deactivation and overheating of the catalyst. The periodic two-step process with flow reversal allowed the production of pure and dry chlorine at a high space time yield. By operating the process at temperatures lower than 400 °C the catalyst deactivation due to  $\text{CuCl}_2$  volatilization was minimized. They suggested that an optimal catalyst design was essential to overcome the dechlorination rate limitation and the HCl

contamination. Dynamic simulations showed that flow reversal rapidly leads to overtemperatures. Cocurrent operation and optimal dilution of the feeds by nitrogen made it possible to keep reactor temperatures between 250 °C and 400 °C.

Opoku-Gyamfi *et al.* (2000) investigated the influence of cycle parameters on periodically operated fluidized bed reactor for CH<sub>4</sub> autoreforming. The foregoing results indicated that under periodic cycling, CH<sub>4</sub> steam reforming proceeded via the interaction of entities derived from the dissociative adsorption of CH<sub>4</sub> and H<sub>2</sub>O leading to the predominant formation of CO<sub>2</sub> and H<sub>2</sub>. CH<sub>4</sub> oxidation on the other hand occurred through the reaction of adsorbed CH<sub>4</sub> and O<sub>2</sub> derivatives to form CO and H<sub>2</sub>O as the major products. At  $\tau=1$  min,  $S_{ox}=0.1$ ;  $\tau=10$  min,  $S_{ox}=0.1$ ;  $\tau=20$  min,  $S_{ox}=0.1$  ( $S_{ox}$  was cycle split, defined as the fraction of time spent in the O<sub>2</sub>-rich region, and  $\tau$  was cycle period), periodic cycling resulted in higher (15% increase) H<sub>2</sub> formation rates compared to steady state operation. Periodic operation offered a more convenient and flexible approach to modulating H<sub>2</sub>/CO ratio during autoreforming than steady state operation.

The operation of a trickle-bed reactor in the pulsing flow regime was well known for its advantages in terms of an increase in mass and heat transfer rates. Boelhouwer *et al.* (2001) mentioned that the advantages associated with pulsing flow might then be utilized to improve reactor performance in terms of an increase in capacity and the elimination of hot spots, while interfacial contact times were comparable to trickle flow. During the periodic operation of a trickle bed, continuity shock waves were initiated in the column due to the step-change in liquid flow rate. This resulted in the division of the column into a region of high liquid holdup and a region of low liquid holdup. At high enough gas flow rates, the inception of pulses took place in the liquid-rich region. Analysis of the performed experiments indicated that besides gas and liquid flow rates, an additional criterion for pulse inception was the available length for disturbances to grow into pulses. For self-generated pulsing flow this resulted in the upward movement of the position of the point of pulse inception with increasing gas flow rate. With liquid-induced pulsing flow this means that higher gas flow rates were necessary to induce pulses as the length of the liquid-rich region decreased.



The direct catalytic cracking of methane into hydrogen and carbon was explored in detail as a potential alternative to steam reforming and partial oxidation to produce hydrogen free of carbon oxides by Monnerat *et al.* (2001). Deactivated catalyst could be regenerated in the oxidative atmosphere. Therefore, the direct catalytic cracking was followed by catalyst regeneration during periodic reactor operation. The temperature strongly affected the conversion and the selectivity of the process towards hydrogen and carbon oxides formations. The influence of cycle time on the time-average hydrogen performance showed a maximum for a cycle of 4 min. The selectivity of carbon oxides were not influenced by the cycle duration. The influence of the cycle split on the time-average hydrogen performance showed that a maximum value was attained cycle split = 0.5. This value corresponded to a symmetric period when the time of cracking was equal to the time of regeneration.

An  $\alpha$ -methyl styrene hydrogenation over Pd/Al<sub>2</sub>O<sub>3</sub> under periodic operation was studied by Turco *et al.* (2001). In this reaction the transport of H<sub>2</sub> from the liquid phase to the Pd surface was largely rate controlling. An attempt to exploit the inertial effects by varying the gas loading in a downflow co-current trickle bed was not successful. On the contrary the periodic modulation in liquid loadings could result in significant increases in rates of reaction even when there was no change in bed temperature as a result of modulation. The improvement probably resulted from inertial effects which allow foaming created at high liquid flow rates to persist when the liquid flow rate was reduced to a low value and the system should have reverted to a trickling regime without foam.

Gutsche *et al.* (2003) studied the effect of the nonlinearity of an isothermal catalytic reactor including an irreversible heterogeneous reaction of the Langmuir-Hinshelwood type on the yield change caused by periodic operation. As found in the case of quasi-stationary periodic operation, global improvements were only obtained if the surface reaction is the rate controlling step. With rising sorption rate limitations, the global enhancement was strongly diminished and attained a value of 1 (no improvement) if the sorption process controlled the overall rate. External mass transfer was found to have a negative effect on the global yield improvements, i.e. the larger the contribution of the external mass transfer to the overall process rate the

smaller the yield improvements. No improvement was obtained for external mass transfer control. Axial dispersion proved to have only a negligible effect on global yield improvements.

Tukač *et al.* (2003) studied the impact of dynamically changing extent of wetted catalyst external surface and intensify mass transfer of gaseous oxygen on catalytic wet oxidation rate of aqueous phenol under periodic modulated liquid feed. They found that periodic operation of trickle-bed reactors significantly increased phenol wet oxidation rate in comparison to reaction rate measured at the steady state operation mode. Temperature effects of an exothermic reaction, periodic wetting of external catalyst surface and improvement in oxygen mass transfer from gas phase to catalyst active sites were strongly influenced by operation parameters like gas and liquid flow rates, inlet temperature and pressure, and by feed modulation parameters, period length and split.

## 2.2 Comment on previous works

From the previous studies about the reaction, there are many researches about the hydroxylation of aromatic by  $\text{H}_2\text{O}_2$  over the TS-1. However there are only some researches about the hydroxylation of benzene by  $\text{H}_2\text{O}_2$  although this is the simple reaction (it yields only two products). From the reviewed literatures, the particle size of TS-1 catalysts had the influence on catalytic activity. It resulted that large zeolite particle were not fully utilized because of pore diffusion limitations. Thus, the hydroxylation reaction might occur primarily on the external surface of catalyst particle. Rate controlling step then would be the film type mass transfer from the liquid phase to TS-1. The periodic switching of flows that controlled the wetting efficiency (which affected the mass transfer rate) should increase the rate of reaction and yield.

Although, the periodic operation could be improved the rate of the hydroxylation of benzene reaction, but the previous studies showed no research in this operation. Thus, the hydroxylation of benzene by  $\text{H}_2\text{O}_2$  using the TS-1 as the catalysts under periodic operation is chosen to studied in this research.