Reverse flow reactor operation for control of catalyst surface coverage
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Reverse Flow Reactor Operation for Control of Catalyst Surface Coverage

Yogi W. Budhi
Stellingen

behorende bij het proefschrift/propositions accompanying the thesis

Reverse Flow Reactor Operation
for Control of Catalyst Surface Coverage
van/by
Yogi W. Budhi

1. Manipulation of the catalyst surface coverage for improved conversion and selectivity substantially requires more frequent flow reversals than the classical reverse flow operation for energy saving does (Chapter 1).

2. A reverse flow reactor should be operated at comparable switching time and residence time in order to manipulate the reactor’s selectivity (Chapter 3).

3. The concept of reverse flow operation with concentration programming provides an engineering tool to control conversion and selectivity, with three benefits: ammonia feedstock savings, increased ammonia conversion, and increased selectivity to NO; a drawback is the decrease of production rate (Chapter 4).

4. The concept of reverse flow operation with reactor side feeding shows a fourfold superior performance: higher conversion of ammonia, higher selectivity to NO, no dead gas volume, and high production rate (Chapter 5).

5. Intensification of a university study program must assure that the students’ residence time distribution for completing their study follows a plug flow model.

6. The concept of periodic reactor operation is natural.

7. So called relaxation oscillation occurs when the cycling time period is much less than the system’s time constant. However, this is not the case during reverse flow operation when operating the reactor at extremely short cycling time.

8. The porosity of a fixed bed can be determined elegantly by a combination of reverse flow operation and cycling of the feed concentration.

9. Joint bachelor-master-doctor programs improve the selectivity to master and doctor degrees as well as the productivity of a university.

10. Assalamu’alaikum is a time-independent greeting.
Reverse Flow Reactor Operation
for Control of Catalyst Surface Coverage

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de
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All rights reserved. No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without the prior written consent of the author.
To my beloved wife Elvi Restiawaty
and my lovely kid Tareqh Al Syifa Elgi Wibisono
with love and gratitude

To my parents, father in law, the memory of my mother in law, my brothers, and my sisters
for their pray and endorsement

This thesis is also dedicated to the innumerable people in the twenty first century who devoted their lives to the advancement of science, technology, and the betterment of the human conditions.
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Catalytic fixed bed reactors usually operate under steady state conditions. Their performance, however, in terms of conversion and/or selectivity might be significantly increased when the operation is carried out under transient conditions. The development of successful operating procedures forms a real challenge, and the application of such procedures can be considered as an important step in process intensification. A typical example of a transient reactor operation is the reverse flow reactor, in which the flow direction is periodically reversed. This causes time-dependent, cyclic behaviour. This type of reactor has ample applications for exothermal catalytic reactions for reason of energy saving.

This thesis addresses a theoretical study and experimental work on reverse flow operation (RFO) for the selective oxidation of NH₃ over Pt/Al₂O₃. The NH₃ oxidation was arbitrarily chosen as a model reaction because it involves interesting selectivity issues as N₂, NO, or N₂O could be the reaction product. Focus was on the development of a transient operation procedure for a fixed bed reactor, which would allow to manipulate the selectivity towards a specific product at high conversion. Basic idea is that the local rates of the catalytic reactions depend on the coverage of the catalyst surface with adsorbed species. This coverage will be affected by regular changes of the flow direction, causing spatio-temporal patterns inside the reactor. The primary goal of this work is therefore to demonstrate that RFO may create dynamic changes of active site coverages, which may influence the reactor’s conversion and selectivity when compared to steady state operation (SSO).

A dedicated experimental set-up for reverse flow experiments was designed and constructed. Steady state experiments were carried out first of all, by operation of the fixed bed reactor in unidirectional flow. During these experiments, the effects of the reaction temperature, oxygen feed concentration, and residence time on the conversion and selectivity were investigated. These results formed the base case to judge if RFO might create potential benefits. The results were also used to assess the kinetics of NH₃ oxidation on the level of elementary reaction steps. A kinetic model from the literature could be applied to describe adequately the steady state data after minor adaptation of some rate parameters.

The time period, after which the flow direction is reversed during RFO, is referred to as the switching time. For manipulation of the catalyst surface coverages it appears necessary to apply switching times in the order of seconds, which is significantly smaller than the order of minutes to hours,
used in the traditional RFO for energy saving. Three different regimes of RFO are distinguished, depending on the ratio $\alpha$ of switching time over residence time: quasi-steady state regime ($\alpha > 1$), dynamic regime ($\alpha \approx 1$), and relaxed steady state or sliding regime ($\alpha < 1$). The latter case induces a dead gas volume in the central part of the reactor. Periodically flushing might form an interesting option to refresh such dead volume with fresh feed. An increase of conversion was indeed found, when comparing RFO plus flushing to regular RFO. The selectivities changed as well. Regular RFO always invokes a conversion decrease in comparison to SSO as was observed during the experiments and validated with model predictions. This major drawback of regular RFO is more pronounced at shorter switching time. It was also found that the selectivity was rather insensitive to changes in the switching frequency. A decrease of the gas flow rate at constant switching time basically shifts the operation regime towards the relaxed steady state regime. The temperature and the oxygen feed concentration may affect the conversion and selectivity during RFO in either positive or negative way, depending on their relative influence. Asymmetric RFO, which means that forward and backward flows last different time periods, induces even a larger conversion decrease, while it slightly influences the selectivity.

A novel concept of RFO with temporarily lower feed concentration was proposed to overcome the conversion decrease during regular RFO. The feed concentration was always lowered shortly before the flow direction was reversed. Next to the switching time, the time period of lower concentration is a crucial variable, which strongly influences conversion and selectivity. The influences of $O_2$ feed concentration, temperature, and amplitude were considered as well. The model predictions and experimental results exhibit clear evidence that RFO with periodically lower feed concentration is appropriate to manipulate the selectivity and to increase the conversion with respect to regular RFO. Values were obtained that were even better than in SSO. The selectivity to NO increased, but the selectivities to $N_2$ and $N_2O$ decreased. However, the reactor’s production rate dropped considerably.

Another novel concept of RFO with reactor side feeding was also studied in order to avoid the conversion decrease during regular RFO. The axial position of the feed appeared an important variable. Residence time and temperature were varied as well to study their influence on conversion and selectivity. Dead gas volumes were eliminated by defining a minimum switching time for each feed position. At minimum switching time, the conversion of $NH_3$ and the selectivity to NO could be significantly increased up to levels that exceed the SSO performance. The opposite holds for the selectivities to $N_2$ and $N_2O$. At larger $\alpha$ values with the feed positions near the reactor center, the conversion of $NH_3$ and the selectivities to $N_2$ and NO decreased, while the selectivity to $N_2O$ increased. With the feed positions near the reactor ends, the conversion of $NH_3$ and the selectivity to $N_2O$ were larger than in the steady state, while the selectivities to $N_2$ and NO were lower.
Samenvatting

Katalytische gepakt bed reactoren werken gewoonlijk onder stationaire omstandigheden. Hun prestaties in termen van conversie en selectiviteit kunnen mogelijk significant worden verbeterd als de operatie wordt uitgevoerd onder transiënte voorwaarden. Zo’n transiënt gedrag valt te realiseren door het cyclisch variëren van de operatiecondities. Het ontwikkelen van succesvolle operatieprocedures vormt een echte uitdaging, en het toepassen van dergelijke procedures kan men beschouwen als een belangrijke stap in procesintensificatie. Een typisch voorbeeld van transiënte reactor operatie is de “reverse flow reactor”, waarbij de stromingsrichting periodiek wordt omgekeerd. Dit veroorzaakt een cyclisch, dus tijdsafhankelijk gedrag. Een dergelijk type reactor is al vaak toegepast voor exotherme katalytische reacties met energiebesparing als doel.

Dit proefschrift behandelt zowel een theoretische studie als experimenteel werk over “reverse flow operation” (RFO) voor de selectieve oxidatie van ammoniak over een alumina gedragen platina katalysator. De NH₃ oxidatie is arbitrair gekozen als modelreactie vanwege interessante selectiviteitsaspecten, omdat N₂, NO, en N₂O het reactieproduct kunnen zijn. De aandacht is daarbij speciaal gericht op het ontwikkelen van een transiënte operatieprocedure voor een gepakt bed reactor, waardoor de selectiviteit kan worden gemanipuleerd naar één specifiek product bij een hoge conversie. Aan de basis ligt het idee dat de lokale snelheid van katalytische reacties afhangt van de bedekking van het katalysatoroppervlak met geadsorbeerde species. Die bedekking wordt beïnvloed door het regelmatig omkeren van de stromingsrichting, hetgeen spatio-temporele patronen in de reactor veroorzaakt. Het primaire doel van dit werk is daarom aan te tonen dat RFO dynamische veranderingen kan creëren van de bedekking van actieve centra, waardoor de conversie en selectiviteit van de reactor worden beïnvloed in vergelijking met stationaire operatie (SSO).

Een op reverse flow experimenten toegespitst experimenteeropstelling werd ontworpen en gebouwd. Hiermee werden allereerst experimenten in de stationaire toestand uitgevoerd door de reactor te bedrijven met doorstroming in één richting. Tijdens deze experimenten werd de invloed van de temperatuur, de voedingsconcentratie zuurstof en de verblijftijd onderzocht op conversie en selectiviteit. De hieruit volgende resultaten vormden een basis om te beoordelen of RFO potentiële voordelen zou kunnen bieden. De resultaten werden ook gebruikt om de kinetiek van de ammoniak oxidatie te beschrijven op het niveau van elementaire reactiestappen. Een kinetisch model uit de literatuur kon worden toegepast om de stationaire data goed te
beschrijven, nadat enige snelheidsparameters een geringe wijziging hadden ondergaan.

De tijdsperiode waarna tijdens RFO de stromingsrichting wordt omgekeerd wordt de schakeltijd genoemd. Om de oppervlaktebedekkingen van de katalysator te manipuleren, blijkt het noodzakelijk om schakeltijden te gebruiken in de ordegrootte van seconden, wat signifikanter kleiner is dan de orde van minuten tot uren, die worden toegepast tijdens de traditionele RFO voor energiebesparing. Afhankelijk van de verhouding $\alpha$ van de schakeltijd tot de verblijftijd kunnen er drie verschillende regimes voor RFO worden onderscheiden: het quasi-stationaire regime ($\alpha > 1$), het dynamische regime ($\alpha \approx 1$), en het glijdend regime ($\alpha < 1$). Het laatste veroorzaakt een dood volume in het centrum van de reactor. Het regelmatig doorspoelen van die ruimte zou een optie kunnen zijn om het dood volume van verse voeding te voorzien. Inderdaad wordt hiermee een conversie-verbetering gevonden t.o.v. normale RFO. De selectiviteiten veranderen eveneens. Normale RFO leidt altijd tot een verlaging van de conversie vergeleken met SSO, zoals uit zowel experimenten als modelvoorspellingen blijkt. Dit evident nadeel van normale RFO wordt ernstiger bij kortere schakeltijden. Waargenomen wordt ook dat de selectiviteiten niet erg gevoelig zijn voor veranderingen in de schakelfrequentie. Een verlaging van het gasdebiet bij constante schakeltijd laat het operatieregime richting het glijdend regime verschuiven. Temperatuur en voedingsconcentratie zuurstof hebben invloed op conversie en selectiviteit, en afhankelijk van hun relatieve bijdrage kan dat positief of negatief zijn. Asymmetrische RFO, d.w.z. met een verschil in duur van de heen- en teruggaande stroming, veroorzaakt nog grotere conversiedaling, terwijl de selectiviteit lichtelijk verandert.

Een nieuw concept, RFO met tijdelijk verlaagde voedingsconcentratie, wordt voorgesteld om de conversieverlaging tijdens normale RFO te vermijden. Kort voor de stromingsrichting wordt omgekeerd werd de voedingsconcentratie steeds verlaagd. Behalve de schakeltijd is nu de periode van verlaagde concentratie een belangrijke variabele met veel invloed op de conversie en de selectiviteit. Het effect van zuurstof concentratie, temperatuur, en amplitude in de voeding werd ook onderzocht. Modelvoorspellingen en experimentele resultaten tonen duidelijk aan RFO met periodiek lagere voedingsconcentratie in staat is om de selectiviteit te manipuleren en de conversie te verhogen t.o.v. normale RFO. Waarden worden verkregen, die zelfs beter zijn dan in de stationaire toestand. De selectiviteit naar NO neemt toe, terwijl die naar N₂O en N₂ afnemen. De productie van de reactor wordt wel behoorlijk kleiner.

Een ander nieuw concept, RFO met voedingen aan de zijkant van de reactor, wordt ook bestudeerd om de verlaagde conversie tijdens normale RFO tegen te gaan. De axiale positie van de voedingen blijkt een grote invloed te hebben. Verblijftijd- en temperatuurinvloeden worden eveneens bestudeerd. Door voor elke voedingspositie een minimale schakeltijd te definiëren, kan het dode
volumen in het reactorcentrum worden geëlimineerd. Verplaatsing van de voeding richting centrum van de reactor leidt bij de bijbehorende minimale schakeltijd tot een significante verhoging van de conversie en de selectiviteit naar NO, zelfs tot waarden die het niveau van de stationaire toestand te boven gaan. Het omgekeerde geldt voor de selectiviteiten naar N₂ en N₂O. Bij grote α-waarden en de voedingsposities dicht bij het centrum van de reactor nemen de ammoniakconversie en de selectiviteiten naar N₂ en NO af, terwijl die naar N₂O toeneem. Met voedingsposities meer in de buurt van de reactoruiteinden wordt een hogere NH₃-conversie en N₂O-selectiviteit bereikt dan in de stationaire toestand, maar nu zijn de selectiviteiten naar N₂ en NO lager.
Chapter 1

Dynamic Operation for Control of Conversion and Selectivity

The first step to knowledge is to know that we are ignorant
Socrates (470 – 399 B.C.)

§ Selective oxidation of ammonia
§ Transient reactor operation
§ Reverse flow reactor operation
§ Aim, scope, and outline of thesis
§ Closure remarks

Summary
It is well established that for exothermic reactions in catalytic fixed bed reactors, reverse flow operation traps energy released by the reaction in the central portion of the bed to produce elevated temperatures. The extensive work on reverse flow reactors has explored its functionality in a wide range of applications, but most of the studies are devoted to the goal of energy savings. In principle, deliberate reactor perturbation can be implemented to any process variable and process operation mode. The latter spans from cycling of the feed concentration, regular admittance of reactant pulses in the feed, and periodically changing the flow direction. In this chapter, the state-of-the-art of reverse flow reactors is discussed for the particular application of manipulation of the catalyst surface coverage during the selective oxidation of ammonia. A general introduction concerning the structure of the thesis and an overview of the challenges of the reverse flow reactor in process intensification will conclude this chapter.
CHAPTER 1. Dynamic Operation for Control of Conversion and Selectivity

The research field of dynamic reactor operation is deliberately devoted to the development of transient operation and control procedures for catalytic reactors with the objective to improve their performance. One great challenge is to increase the reaction's conversion or selectivity through manipulation of the catalyst's surface coverage or storage capacity by suitable perturbations of the reactant inlet conditions or by dedicated flow reversals. Transient kinetic studies are performed to identify the relevant elementary reaction steps and to quantify the kinetic rate coefficients that are used in supporting modeling studies. One of the most interesting applications concerns the reduction of laughing gas (N₂O) during the selective oxidation of ammonia in nitric acid plants by control of the relevant elementary reaction steps. Basically, this might be achievable by a dedicated operation procedure for a fixed bed reactor with periodic flow reversal, aiming at selectivity improvements with respect to the desired product, or avoiding that the undesired products are detected at the reactor outlet. From this research emerged the idea that under deliberately and artificially created unsteady state conditions, it is possible to increase the productivity, conversion, or selectivity of a catalytic process as a whole when compared to steady state performance. This issue is interesting from a viewpoint of process intensification (Stankiewicz and Moulijn, 2004).

The scientific literature in this field is mostly theoretical and aims at both structuring and analyzing mathematical models of unsteady state catalytic processes. In this thesis, the theoretical and applied aspects of artificially created unsteady conditions in catalysis, particularly in a fixed bed reactor with flow reversal are discussed. Novel concepts to the application of unsteady state catalysis for an advanced reverse flow reactor are proposed for manipulation of conversion and selectivity.

This chapter is intended to enable the reader to develop a clear understanding of the aim and structure of the thesis. It provides a general overview concerning the research project of reverse flow reactors for manipulation of conversion and selectivity. The discussion commences with the selective oxidation of ammonia, which is the model reaction throughout this study. Following topics are: transient reactor operation, reverse flow reactor operation, and finally aim, scope, and outline of this thesis.

SELECTIVE OXIDATION OF AMMONIA

The oxidation of ammonia (NH₃) with air to nitric oxide is the first step in the production of nitric acid and subsequent manufacturing of fertilizers. The ammonia oxidation step may yield the products nitrogen (N₂), nitric oxide (NO), and nitrous oxide (N₂O) with temperature dependence on conversion and selectivity. The subsequent step is the oxidation of nitric oxide to nitrogen
dioxide, which is followed by absorption in water to give a solution of nitric acid. Figure 1-1 represents the typical ammonia burners of a dual-pressure type in a nitric acid plant, in which the absorption takes place at a higher pressure than the oxidation stage. The dual-pressure plant provides the efficient operation for nitric acid manufacturing with a minimum catalyst loss.

The industrial production of NO from NH₃ over catalytic platinum/rhodium gauzes, known as the Ostwald process, is currently performed in the Netherlands by DSM AGRO, Yara, and Kemira Agro. Extremely short contact times, elevated temperatures, and intermediate pressure (typically over 1073-1173 K and 5 atm) are applied. One tries to reach 100% NH₃ conversion in order to avoid downstream formation of NH₄NO₃. The actual NH₃ conversion of the process over platinum group metal is around 95-97% (Perez-Ramirez et al., 2004). The selectivity to NO is around 96% if that high reactor temperature is maintained. The selectivity to N₂O is 1.5-2%, and the remainder is N₂. Under 773 K, the reactor would produce mainly N₂, which indicates that the reaction selectivity is strongly depending on the applied temperature.

Apart from the selectivity, a high temperature is also required in order to activate new gauzes in the reactor. Depending on the applied process pressure, the lifetime of gauzes is in the order of 2-8 months. They suffer considerably from the necessary high temperature because platinum is oxidized into platinum oxide, which evaporates. The corresponding rhodium enrichment of the gauzes causes a decrease of the NO selectivity from 96 to 92%. The selectivity to N₂ increases accordingly, while the selectivity to N₂O remains at the level of 1.5-2%.

The undesired by-product of N₂O requires a treatment of the reactor effluent in some stage of the production process in order to avoid emission of the greenhouse gas N₂O. In Europe, the N₂O emission comes from various sources as shown in Figure 1-2. A single N₂O molecule is 310-times more effective in trapping heat in the atmosphere than a CO₂ molecule. World wide, nitrous
oxide is responsible for about 10% of the emission of greenhouse gases. In the European union, the chemical industry is responsible for about 23% of the N₂O emission, with the production of nitric acid (the fertilizer industry) as the major contributor. Eliminating the N₂O emissions of a large nitric acid plant can offer a greenhouse gas emission reduction of 1 Mton CO₂-equivalents (Website 2).

A known, but not very clean end-of-pipe technology involves non-selective catalytic reduction of both NOₓ and N₂O in the off-gas. Other end-of-pipe technologies, still subject of experimental studies, concern the addition of a reducing component like methane or propane at a significantly lower temperature. Such an approach is expensive, as it cannot be combined with de-NOₓ, meaning that a separate reactor is required. Treatment of the reactor effluent in a catalytic reactor, placed within the ammonia oxidation reactor, seems a promising solution, which will be tested by several producers on plant level. The recovery of platinum oxide involves capture by fine-woven palladium gauzes and dust filtration. Palladium gauzes and filter bags are recycled by the metallurgical industry.

Ammonia oxidation over the years has become a highly optimized and balanced process. By consequence it is hard to implement in existing plants proposals for improvement, even if they are proven technology. In this respect, the current study should be considered as providing a long-term solution that could be applied for new plants. Implementation in existing processes, however, could become a serious option if the N₂O formation would be suppressed, and moreover the NO selectivity would be extra increased at the expense of the N₂ formation. In this respect, a further investigation of the mechanism and kinetics of the ammonia oxidation, notably the formation of nitrous oxide, would be very useful.
CHAPTER 1. Dynamic Operation for Control of Conversion and Selectivity

TRANSIENT REACTOR OPERATION

Most chemical processes are designed to operate at a steady state condition. In practice, some of the general process variables vary with time, but the steady state design is based on the average values of these fluctuating quantities (Douglas and Rippin, 1966). Past work, almost entirely theoretical, has shown that periodic reactor operation can in some cases produce more reaction products or a more valuable distribution of products than a steady state reactor (Silveston et al., 1995; Silveston, 1998). Moreover, transient methods have been suggested to study chemical kinetics experimentally (Bailey, 1973).

Transition from the usual steady state mode of continuous processes toward forced unsteady state conditions has been discussed in chemical engineering literature since the beginning of the 1960s (Douglas and Rippin, 1966; Bailey, 1973; Watanabe et al., 1981). In principle, forced unsteady state conditions can be created by periodic variations of temperature, composition, or other inlet process parameters. Accumulated experience of unsteady state behaviour allows an affirmative answer to the question: ‘periodic operation of chemical reactors: are global improvements attainable?’ More efforts, however, are needed to elucidate what type of unsteady state conditions will provide maximum effect and how large its value will be (Yadav and Rinker, 1989).

Nowadays, transient operations open new ways in process intensification, which may offer considerable advantages for the performance of a process if a dedicated procedure can be developed. In practice it means that permanently one or more process variables are perturbed according to some schedule, which either disturbs the steady state of a process or even may prevent that a process becomes steady. In the case of heterogeneously catalyzed gas reactions in a fixed bed reactor, such artificially invoked transient behaviour provides opportunities to create dynamic changes of the catalyst surface coverage, which affect the rates of the catalytic reactions. This principle has been widely explored by applying cycling of the feed for improvement of reactor conversion or selectivity (Silveston, 1998).

In principle, perturbations can be applied to any process variable, such as temperatures, concentrations, and flow rates. Well-known strategies, all of them aiming at an improvement of the performance of catalytic reactors, are:

- **Cycling of the feed** (Silveston et al., 1995), which concerns periodically changing the reactor’s feed composition in order to enhance local reaction rates inside the reactor. On a laboratory scale, this method has been shown beneficial concerning conversion and/or selectivity for many reactions, but only if the performance is at a low or moderate level. A high frequency cycling of the feed has been shown by Hoebink et al. (1999) to provide much more detailed information on the kinetics of CO oxidation than could be obtained from steady state experiments.
• **Regular admittance of reactant pulses in the reactor feed in order to diminish catalytic inhibition effects that cause lower reaction rates:** It has been applied to improve the reactor performance by regeneration of catalysts, deactivated due to poisoning (Weerts et al., 1996).

• **Periodically changing the flow direction through the reactor, better known as reverse flow reactor operation:** This principle has been shown beneficial for exothermic reactions from a viewpoint of energy saving (Boreskov et al., 1982; Boreskov and Matros, 1983; Matros and Bunimovich, 1996). Considerable lower feed temperatures can be applied while maintaining the same reactor temperature. The basic mode of operation is deceptively easy and does not include forced oscillation of inlet gas temperature or composition, but simply comprises a periodic reversal of cold gas flow to a preheated fixed catalyst bed.

Improvements of conversion and/or selectivity by cycling feed composition or by admittance of pulses in the reactor feed are ascribed to temporary changes of the coverage of the catalyst’s active sites by reacting species. The most favourable situation is obtained if the surface coverages are in agreement with the stoichiometry of the desired reaction as it occurs on the catalyst surface. The catalyst’s activity drops considerably when one species is abundant on the surface. In the case of multiple reaction products, the actual surface coverages determine the product distribution. Periodic flow reversals are another manner to affect the coverages of active sites. In principle, it could be possible to eliminate an undesired product by reversing the flow when that component is detected at the reactor outlet. In this contribution, possible operation procedures for fixed bed reactors in reverse flow mode are explored.

Three regimes are known when operating a reactor in a transient way (Matros, 1989):

• In the so-called quasi-steady state regime, the time scale of the transient is large compared to the time scale of the reaction/reactor. The process can easily respond to the perturbation and may be considered as mainly steady with respect to the actual status of the transient. The time-average behaviour will deviate (in positive or negative sense) from the behaviour obtained in the steady state if the system is non-linear.

• The relaxed steady state regime or sliding regime concerns very fast perturbations that do not cause any disturbance of the reaction/reactor, as the dynamics of the process are too slow. This situation corresponds to the real steady state. The term of relaxed steady state may be used interchangeably, reflecting the wide range of terminology used in the current literature.

• In between is the dynamic regime, where transients and process have comparable time scales. Here perturbations could cause resonance effects due to the non-linear behaviour of the whole system. This region seems most interesting.
The three regimes are illustrated in Figure 1-3, where the responses of the turn-over frequency ($N_{qss}$ for quasi-steady state, $N_{dyn}$ for dynamic, or $N_{sl}$ for sliding) of a catalyst have been plotted versus time. The gas phase concentration ($C_{A,in}$) shows square wave perturbations with different time scales (Hoebink et al., 1995). Steady state ($N_{ss}$) and time-average ($N_{tavg}$) values of the turn-over frequency are shown as well. In the quasi-steady regime, $N_{qss}$ readily reaches the value that corresponds with the actual gas phase concentration (see Figure 1-3a). For the particular kinetics that were adopted for this case, the time-average value ($N_{tavg}$) of the turn-over frequency is lower than the steady state value ($N_{ss}$), which would be obtained if $C_{A,in}$ was maintained at the average value of the perturbations. In the dynamic regime, the turn-over frequency response ($N_{dyn}$) does not reach the value that corresponds with the actual gas phase concentration (see Figure 1-3b). The system is maintained in an unsteady state. Before the response reaches the steady state value, the system is perturbed again. For fast perturbations, the turn-over frequency response ($N_{sl}$) is rather independent of the actual gas phase concentration, and its value corresponds with the time-average value of the concentration (see Figure 1-3c).

Transient operation is more complicated and probably more expensive than steady state operation. Consequently, if increased conversion or selectivity is the goal, it could be achieved more cheaply by increasing reactor size or the amount of catalyst employed. Under these circumstances, changing from steady state to transient operation could only be justified by a large increase in catalyst activity, perhaps 100% or more (Silveston et al., 1995). It should be kept in mind, however, that transient operation might show a performance that never can be realized under steady state.

**REVERSE FLOW REACTOR OPERATION**

Among the various options for transient operation, periodic operation offers the combined benefits of a permanent unsteady-state regime and a constant time-average regime. Periodically changing the flow direction through the reactor, better known as Reverse Flow Operation (hereinafter referred to as RFO), has not yet been widely applied for improvement of conversion or selectivity, but was shown beneficial for exothermic reactions from a viewpoint of energy saving. The use of the reverse flow principle as transient operation procedure for a catalytic reactor becomes interesting by the combination of dynamic properties at a microscale (catalyst) and at a macroscale (reactor). It may produce more favourable concentration and temperature profiles for the catalytic process (Ferreira et al., 1999).
Figure 1-3.
Square wave gas phase perturbations ($C_{A,in}$) and rate responses ($N_{qss}$, $N_{dyn}$, $N_{sli}$). Note different time scales. Steady state ($N_{ss}$) and time-average ($N_{avg}$) rates are shown as well (Hoebink et al., 1995).
Figure 1-4 shows a schematic illustration of a fixed bed reactor for a steady state, once-through operation (a) and for a reverse flow operation (b). Successful RFO applications on an industrial scale are the oxidation of SO$_2$ into SO$_3$ and the oxidation of volatile organic components in effluents. Some other processes are under development, such as methanol synthesis and methane oxidation. A recent and excellent review gives a detailed overview of the advances that have been made in reverse flow operation. Many of these are heterogeneously catalyzed processes carried out in reactors packed with particles of a solid catalyst in between outer zones of inert particles. The advantages of such structured solid phases are not only optimized flow distribution patterns and the reduction of pressure drop. New alternatives in the conceptual design of the reactors are possibly the use of the solid catalyst both as a reaction accelerator and a heat recuperator (Matros and Bunimovich, 1996).

The advantages of the so-called forced transient operation have been highlighted and enumerated some decades ago. The concept of RFO was refined and then extended to catalytic reactors by Boreskov et al. (1982). An implementation was made for SO$_2$ oxidation (Sapundzhiev et al., 1988, 1990; Bunimovich et al., 1990, 1995; Xiao et al., 1999), which was continued by the installation of a successful process on an industrial scale (Matros, 1990). Ferreira et al. (1999) proposed reverse flow operation as a way to decrease the hot spot temperature and to obtain a more favourable temperature distribution along the bed for o-xylene oxidation to phthalic anhydride. The reverse flow operation can also be successfully applied for selective reduction of NOx by ammonia (Bobrova et al., 1988; Jirat et al., 1999; Matros et al., 1999).

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**Figure 1-4.**
Schematic illustration of a fixed bed reactor: (a) once-through reactor operation; (b) reverse flow reactor operation. In the reverse flow operation, the flow passes 1-2-R-3-4 during the first half of each cycle, and during the second half of each cycle, the flow passes 1-2'-R-3'-4.
Matros (1989) studied methanol synthesis under reverse flow operation, followed by Thullie and Burghardt (1990), and Neophytides and Froment (1992). Vanden Bussche et al. (1993) considered a one-dimensional heterogeneous model for this application. Various levels of transient modeling are compared. The most sophisticated model, accounting for mass and energy capacities in both solid and gas phase is used to assess the influence of a number of operating parameters. Much advancement has been gained until this moment in a wide range of process industries. More details on the potential of reverse flow operation have been reported in an excellent overview by Matros and Bunimovich (1996).

A transient operation according to the reverse flow principle gives rise to complicated dynamic behaviour of the fixed bed reactor, as has been reported on several occasions for the classical application of energy saving (e.g. Salinger and Eigenberger, 1996; Khinast and Luss, 2000). The complexity is due to the non-linear dynamics of the whole system, caused by the usually non-linear reaction kinetics on the scale of a catalytic active site, in combination with heat transfer aspects on the scale of the reactor. Even a single, first order, exothermic reaction, carried out in a reverse flow reactor, may show five regions with different bifurcation diagrams, the Damköhler number being the bifurcation parameter (Khinast and Luss, 2000). The existence of stable periodic states depends on the bifurcation parameter value and on the route that leads to the specific position in the bifurcation diagram. Knowledge of the bifurcation behaviour is important for reactor design and reactor control in order to avoid unstable operation. It is also important to assess a safe reactor start-up procedure, which includes a start-up period as short as possible.

AIM, SCOPE, AND OUTLINE OF THESIS

The steady state operation of a fixed bed reactor is most common in industrial applications. Such kind of operation plays a dominant role in chemical engineering due to the ease of mass and energy transformations and the ability of set point control. Nevertheless, it is very unlikely that steady state operations produce the best in conversion and selectivity. Since progress in automatic process control nowadays brings essentially every forcing function within reach, there is no need to maintain the process steady state from that point of view. Such tendency is also backed-up by the increase of computational capabilities, which indicates that full-transient modeling could be implemented in more sophisticated control strategies. Also the reactor perturbation is still possible for unsteady state operations if dedicated procedures and cycle times are within reasonable bounds. In a reverse flow reactor, the flow direction is abruptly reversed each time a certain time period, e.g. the switching time, has passed.
The work described in this thesis is part of a research project funded by Novem (the Netherlands Agency for Energy and Environment), STW (Dutch Technology Foundation), and Quality for Undergraduate Education Project, Chemical Engineering Department, Institut Teknologi Bandung, Indonesia. The project predominantly aims to develop procedures for transient reactor operation, notably the application of reverse flow reactors, in order to reduce the emission of the greenhouse gas nitrous oxide during nitric acid manufacturing. Basic idea is that periodic reversals of the flow direction through a fixed bed reactor induce spatio-temporal patterns of both the gas phase concentrations and the adsorbed species coverages on the catalyst surface. The latter affect directly the rates of the catalytic reactions, which dictate the conversion of reactants and the selectivity towards products.

This work focuses on the transient operation procedure for a reverse flow reactor, which is the vitally important tool of engineering to perturb the catalyst surface coverage. The most important goal in this thesis is to determine a proper procedure, which may contribute to a more efficient use of catalyst leading to a better conversion, selectivity, and productivity. In general, one can classify RFO into two major groups, viz. energy saving and kinetic applications. The former has major industrial implementations. The latter, however, has got only limited attention and requires considerations, which are completely different. Conversion and selectivity manipulation issues are most predominant, and reverse flow operation is just one of several possible perturbation techniques. Such an approach requires a time scale, which is completely different to the application of reverse flow operation for energy saving. Hence, a complete and accurate set of research involving kinetic and mathematical modeling, simulation, and laboratory experiment is essential for the development of a successful operation procedure. The architecture and construction of the thesis are shown schematically in Figure 1-5 as a reverse flow diagram.

This thesis presents the experimental investigation of a reverse flow reactor on a laboratory scale for the selective oxidation of ammonia (NH₃) to produce either nitrogen (N₂), nitric oxide (NO), or nitrous oxide (N₂O). The NH₃ oxidation was arbitrarily chosen as a typical reaction as it involves selectivity issues because of various products. The primary goal is to demonstrate that reverse flow operation may create dynamic changes of active site coverages, which might change the conversion and selectivity when compared to steady state, once-through operation.

In Chapter 2, the experimental set-up for reverse flow reactor studies is introduced. Experimental procedures, analytical equipment, and catalyst properties are discussed as well. It also presents the experimental results on steady state, once-through operation for the selective oxidation of NH₃ over Pt/Al₂O₃ catalyst in a fixed bed reactor. These results will be used as a reference to judge the potential of reverse flow reactor operation for NH₃ oxidation.
**Mathematical Modeling**

*Governing equations for gas phase and solid phase*
- Transient plug flow model
- Ignoring pressure drop
- Axial dispersion for stability

**AIM**
provide a model for simulation

**Experimental Study**

*Activity to collect data from the experimental setup*
- Data collection
- Data treatment & analysis

**AIM**
compare model and experiments, and verify the developed model

**Reactor Design**

*Design an appropriate reactor for experimental studies*
- Basic to detailed design
- Experimental setup
- Design criteria

**AIM**
provide an experimental setup required to conduct experiments

**Simulation**

*Observe the model behaviour during reverse flow operation*
- Software package FlexPDE

**AIM**
identify the effect of flow reversal on conversion and selectivity and develop novel concepts of operation showing most benefits

**Figure 1-5.**
Various aspects of this research, depicted as a reverse flow reactor model.

**Chapter 3** describes the simulation and experiments with a reverse flow reactor, which is referred to as “regular reverse flow operation”. It is important to notice that experiments have to be carried out at short cycle times because the manipulation of the catalyst surface coverage for improved conversion and selectivity requires more frequent flow reversal than the
classical reverse flow operation for energy saving does. The consequences of short cycle times are discussed and lead to new RFO concepts, to be considered in the next chapters.

In Chapter 4, a novel concept of reverse flow operation, so-called RFO with “temporarily lower feed concentration” is considered. Here, the feed concentration is periodically lowered just before the flow direction is reversed. It prevents a major outflow of unreacted feed after switching the flow direction. This operation concept overcomes the drawback of regular reverse flow operation at short cycle times.

Chapter 5 covers another novel concept of reverse flow operation, so-called RFO with “reactor side feeding”. The feed gas does not enter the reactor at position $z = 0$ (flow from left to right) or at $z = 1$ (flow from right to left) as usual, but at some axial coordinates in between. The reactor outlets still flow out from the usual positions at $z = 0$ or $z = 1$, depending on the flow direction. This concept improves the reactor performance by a combination of reactor zones with “reversed flow” and with “interrupted flow”.

Finally, the general conclusions and recommendations are the subject of Chapter 6.

**CLOSURE REMARKS**

Reverse flow operation in a fixed bed reactor might be considered as an engineering technique for control of heat propagation and catalyst surface coverage manipulation. The study of reverse flow reactor for selectivity manipulation creates an entirely new class of dynamic operation, which will be presented comprehensively in the following chapters.
Chapter 2

Reactor Modeling, Experimental Set-up, and Steady State Experiments

It isn’t that someone can’t see the solution. It is that someone can’t see the problem.

G.K. Chesterton

§ Introduction
§ Definitions
§ Reactor modeling
§ Kinetics of ammonia oxidation
§ Software development
§ Pre-experiments
§ Steady state experiments
§ Concluding remarks

Summary
The selective oxidation of NH₃ to produce either N₂, NO, or N₂O was chosen as a model reaction because of its selectivity issue. Reactor modeling and simulation of steady state operation were performed based on elementary reaction steps. A catalytic fixed bed reactor and a dedicated experimental set-up were designed to carry out the steady state experiments. The experimental data will be used for a comparison to reverse flow operation (RFO), which aims to judge if RFO may create potential benefits. In the steady state experiments, effects of reaction temperature, oxygen concentration, and residence time on the NH₃ conversion and the selectivities towards N₂, NO, and N₂O are discussed.
The first chapter focused on the general overview of selective oxidation of ammonia as a model reaction in this research, the concept of transient reactor operation for manipulation of conversion and selectivity focusing on reverse flow operation, and the aim of this thesis. In Chapter 2, a number of new terminologies used throughout this thesis are defined, followed by more details about the reactor model, software development, and reactor simulation. Last but not least, the functioning of the experimental set-up is described, followed by the data from steady state experiments as base conditions to compare with the results from the reverse flow operation.

INTRODUCTION

Over the past ten years, reactor development has focused on improving selectivity for heterogeneously catalyzed gas phase processes in fixed bed reactors. The improvement methodology is quite general with process intensification (Stankiewicz and Moulijn, 2004), process miniaturization (Schouten et al., 2002; Rebrov et al., 2003), and transient or dynamic operation (Silveston et al., 1995; Hoebink et al., 1999) as the key elements. The latter plays an important role at all levels of process improvements that cannot be achieved by steady state operation. The transient processes are at the apex of chemical reaction engineering due to involvement of accumulation effects next to convection, dispersion, and reaction as occurs in a steady state. This chapter outlines how reactor modeling and simulation were done, describes the experimental set-up, and discusses the results of steady state experiments for later comparison to reverse flow operation.

DEFINITIONS

The following glossary of definitions and terminologies are used throughout this thesis:

Asymmetric operation of a reverse flow reactor is defined as RFO while the time periods of forward and backward flows are different. When the time periods are the same, it is considered as symmetric operation.

Conversion is the mole amount of reactant, which is converted into product per mole of reactant fed to the reactor. Under transient operation, the conversion is calculated as time-average value over a complete cycle.

Cycle time of a reverse flow operation is the time period required to repeat a flow reversal into the same flow direction.
Dead gas volume is the gas trapped inside the reactor, as caused by reverse flow operation at a switching time less than the gas residence time.

Dynamic regime is defined as a condition during reverse flow operation, in which the switching time of flow reversal is near to the gas residence time of the same reactor, operated under steady state, once-through operation.

Flushing method is a reverse flow operation mode that regularly refreshes the trapped gas in the centre part of the reactor after a certain number of flow reversals by a short period of unidirectional flow.

Minimum switching time is the minimum time required to pass the fixed bed part between the two inlet positions in order to avoid a dead gas volume during reverse flow operation with reactor side feeding.

Regular reverse flow operation (regular RFO) is defined as reverse flow operation with inlets and outlets at the outer ends of the reactor body.

Productivity is defined as the conversion of reactant times the selectivity.

Production rate is defined as the number of moles of product per unit time.

Quasi-steady state regime is defined as a condition during reverse flow operation, in which the switching time of flow reversal is much larger than the gas residence time if the same reactor is operated under steady state, once-through operation.

Reactor side feeding concerns a fixed bed reactor with periodic flow reversals, while the feed positions are placed on the side of the reactor and the effluent positions are at the outer ends.

Relaxed steady state regime or sliding regime is defined as a condition during reverse flow operation, in which the switching time of flow reversal is less than the gas residence time if the same reactor is operated under steady state, once-through operation.

Residence time is the time required for the gas to pass the reactor. For steady state, once-through operation, it is equal to the reactor volume over the volumetric flow rate. For reverse flow operation, the residence time of the gas is not a single fixed value, but it shows a distribution.

Reverse flow reactor (RFR) is defined as a fixed bed reactor, in which the flow direction is periodically reversed after a certain switching time has passed.

Selectivity is defined as the amount of mole of product per mole of reactant converted in the reactor, corrected by stoichiometry. In transient operation, the selectivity is calculated as time-average value over a complete cycle.
Steady state, once through operation is an antipode to reverse flow operation, the flow always passing the reactor in one direction.

Switching time is the time period after which the flow direction is reversed. It is half of the cycle time when the time period is symmetric.

Temporarily lower feed concentration (TLFC) is a reverse flow operation mode, in which the feed concentration of a certain component is intentionally lowered before the flow direction is reversed. This mode avoids the feed concentration losses shortly after reversing the flow direction.

Time-average value is a mean value (concentration, conversion, selectivity, productivity), which is calculated over one full cycle.

REACTOR MODELING

The reverse flow reactor is a relatively new subject of interest. Rather than designing an actual catalytic process, a number of studies are related to mathematical modeling and simulation, which is aimed at describing the major phenomena occurring in a reverse flow reactor (Matros and Bunimovich, 1996). Apparently, several simple models are capable to describe qualitatively the moving temperature and concentration profiles observed during reverse flow operation (Froment and Hofman, 1987; Kiselev et al., 1988; Matros, 1989; Matros and Bunimovich, 1996).

Flow reversal leads to periodic movement of temperature and concentration fields. Therefore, transient terms related to the temperature and concentration of the fixed bed reactor should be included in heat and mass balances. The volumetric heat capacity of a solid catalyst is commonly three orders of magnitude larger than that for a gas (Matros and Bunimovich, 1996). Taking this into account, heat accumulation in the gas phase can be excluded for a simple model. This factor influences the reactor behaviour only at the very beginning of each reversal period.

To model a reactor, a set of mathematical equations is required, which expresses the behaviour of the reacting system under various operating conditions. The purpose of modeling is to develop thorough and detailed information on a process, which then can be used for predicting the reactor behaviour, for optimizing design and operation of the process, and eventually for selection among competing novel concepts. The model should allow predictions of the performance for a wide variety of designs and operating conditions. If possible, it also covers conditions beyond regular operations to predict start-up, off-specification, turndown, and unsafe situations. Such a model should be based primarily on fundamental principles of conservation law, reaction engineering, and reactor hydrodynamics. It should use the
minimum number of adjustable/experimental parameters and be solved by standard mathematical routines requiring minimum execution time. Developing suitable mathematical models in combination with specific experiments leads to a deeper insight into the process. This is applied to develop new reactors or alternative operating principles.

FIXED BED REACTOR

One common configuration in the industrial practice of a catalytic reaction is the fixed bed reactor, which consists of stationary solid catalyst particles through which the reacting fluid flows at certain operating conditions. It is most widely used for gas phase reactions in large-scale production. Although the local flow characteristics in such a reactor are really complex, the macroscopic flow pattern can often be approached as plug flow. The analysis of these reactors spans from the microscale, with the pellet and its pore structure where the phenomena of reaction and diffusion occur, to the macroscale, with the geometry and the characteristics of the reactor bed where the phenomena of heat and mass convection, dispersion, and transfer occur (Matros and Bunimovich, 1996; Andrigo et al., 1999).

In the case of a fixed-bed reactor, the transient reactor behaviour is more difficult to predict. The development of adequate dynamic models is important for automation and optimizing control, process optimization, planning start-up and shut-down, and changes in operating conditions as required for different feed stocks or the necessity to vary product quality. Such activities are only feasible when good dynamic models of reactors are available (van Doesburg, 1974). A typical fixed bed reactor is shown in Figure 2-1. The catalyst particles are loaded as a bed inside the tubular reactor and retained by sintered quartz plates acting as gas distributors.

![Figure 2-1. Schematic presentation of a fixed-bed axial flow reactor. Reactants enter at \( z = - \infty \) products leave at \( z = + \infty \), reaction zone extends from \( z = 0 \) to \( z = 1 \).]
MODEL ASSUMPTIONS

In order to develop the mathematical model and to perform simulations with it, some assumptions are required to simplify the problem without ignoring the major key characteristics. The following assumptions were applied to the model.

- A dynamic, heterogeneous, one-dimensional reactor model was assumed to describe the performance of the reverse flow reactor for reason that selectivity issues require the involvement of continuity equations on the catalyst surface.

- Ideal gas behaviour was assumed at the operating conditions with the physical properties independent of temperature and pressure.

- The kinetic model of ammonia oxidation was considered on the basis of elementary steps, since dynamic features are involved in RFO.

- During preliminary simulations, an imposed gas phase temperature profile along the reactor axis was applied (see Figure 2-2). This profile was calculated for one case, involving heat balances, and it was assured that a permanent cyclic regime had been established. Note that the reactor wall temperature and heat loss through the reactor wall are irrelevant if the temperature profile is known. Therefore, only continuity equations have to be used without accounting for the energy balances. This simplification is based on the consideration of complexity when working on a full elementary step model of NH₃ oxidation, which affects the stiffness of the system of partial differential equations, coupled with ordinary differential equations and algebraic equations. In fact, any temperature profile could be applied by adjusting the heat loss through the reactor wall.

- Reactant adsorption and product desorption were assumed not to affect the gas velocity in the reactor due to dilution with an inert gas.

![Figure 2-2. Imposed temperature profile along the reactor axis as used in the preliminary simulations.](image-url)
• The fixed bed reactor was considered as a plug flow reactor, but an axial dispersion term was deliberately included for numerical stability (Sayer and Giudici, 2002).

• The pressure drop along the reactor bed was ignored in view of the chosen catalyst pellet size, so the momentum balance was not considered.

• Net production of moles by reaction was ignored because of dilution with inert. This means that the terms of mean residence time, space time, and reciprocal space velocity can be interchangeably used.

GOVERNING EQUATIONS

Froment and Bischoff (1990) have already classified fixed-bed reactor models into two categories: pseudo-homogeneous and heterogeneous. Pseudo-homogeneous models do not explicitly account for the presence of the catalyst, in contrast with heterogeneous models, which lead to separate conservation equations for fluid and catalyst. Developing this model for a RFO requires some adaptations depending on the type of reactor configuration.

Table 2-1 shows the mathematical modeling for a reverse flow reactor. Flow reversal leads to transient behaviour, which means that the accumulation term should be incorporated in the continuity equations. In principle, convection is the only fundamental movement of the fluid inside the fixed bed reactor. Therefore, the fixed bed reactor was considered as a plug flow reactor. The dispersion coefficient was set to the value $10^{-7}$ m$^2$ s$^{-1}$ and it was verified that this small value did not affect the obtained simulation results. Hayes and Kolaczkowski (1997) showed that a plug flow model would provide similar results for a fixed bed reactor as a dispersed plug flow model. The source term includes the reaction rates on the basis of elementary reaction steps. The model complexity largely increases when the kinetics are involved on the level of elementary steps, which may induce highly non-linear behaviour. The continuity equations for the gas phase and the solid phase are written in Equations 2-1 till 2-4. The kinetic scheme is discussed in the next section.

In a reverse flow operation, the linear velocity of the gas, $u_s$, changes in sign for every $t_s$ seconds, with $t_s$ being the time period between subsequent switches of the flow direction. When the reactor inlet is at coordinate $z = 0$ (forward flow), the linear velocity is defined as a positive number. On the contrary, the linear velocity is negative when the reactor inlet is at coordinate $z = 1$ (backward flow). The linear velocity changes due to flow reversal are shown in Equations 2-5 and 2-6, respectively, where $u > 0$ is the absolute value of the linear velocity, and $n = 1, 2, \ldots$ is the number of cycles (Matros and Bunimovich, 1996).
Table 2-1. Model equations for the heterogeneous one-dimensional model.

Mass balances for gas phase component \( i \) (\( i = \text{NH}_3, \text{O}_2, \text{N}_2, \text{NO}, \text{N}_2\text{O}, \text{H}_2\text{O} \)):

\[
\frac{\partial p_i}{\partial t} + \frac{u_s}{\varepsilon_b L_r} \frac{\partial p_i}{\partial z} = \frac{D_{ef}}{L_r^2} \frac{\partial^2 p_i}{\partial z^2} + \frac{\Phi p_b}{\varepsilon_b} RT \sum r_k \tag{2-1}
\]

Mass balances for species \( j \), adsorbed on the catalyst surface (\( j = \{\text{NH}_3\}, \{\text{NO}\}, \{\text{O}\}, \{\text{OH}\}, \{\text{N}\} \)), with \( \{ j \} \) as top site, \( (j) \) as hollow site):

\[
\frac{d \theta_j}{dt} = \sum r_k \tag{2-2}
\]

\[
\theta_{0s}^t = 1 - \sum \theta_{js}^t \tag{2-3}
\]

\[
\theta_{0s}^{hs} = 1 - \sum \theta_{jhs} \tag{2-4}
\]

Velocity changes due to flow reversal:

\[
u_s(t) = \kappa(t) u \tag{2-5}
\]

\[
\kappa(t) = \begin{cases} +1 & \text{at } t \in [2(n-1)t_s, 2(n-0.5)t_s] \\ -1 & \text{at } t \in [2(n-0.5)t_s, 2nt_s] \end{cases} \tag{2-6}
\]

Initial conditions:

\[
p_i = p_{is}^{ss} \quad \text{at } t = 0, z \in [0,1] \tag{2-7}
\]

\[
\theta_j = \theta_{js}^{ss} \quad \text{at } t = 0, z \in [0,1] \tag{2-8}
\]

Boundary conditions, \( t > 0 \):

\[
\left. \frac{\partial p_i}{\partial z} \right|_{z=0} = \frac{1 + \kappa(t)}{2} \frac{u_s L_r}{D_{ef}} (p_i^0 - p_i) \tag{2-9a}
\]

\[
\left. \frac{\partial p_i}{\partial z} \right|_{z=1} = \frac{1 - \kappa(t)}{2} \frac{u_s L_r}{D_{ef}} (p_i^0 - p_i) \tag{2-9b}
\]

Time-average outlet concentration:

\[
\bar{C}_i = \frac{1}{t_c} \left[ \int_0^{t_s} C_i(t) \bigg|_{z=1} dt + \int_{t_s}^{t_c} C_i(t) \bigg|_{z=0} dt \right] \tag{2-10}
\]
The steady state situation in a reactor without flow reversal was used as the initial condition for the continuity equations, shown in Equations 2-7 and 2-8. The arbitrary assumption was taken in order to save CPU time, because the steady state concentration profile would be a reasonable first estimate of the situation under conditions of flow reversals at low frequency.

For the dispersed plug flow model, the use of Danckwerts boundary conditions is required, which are shown for the gas phase components as written in Equation 2-9. Because the flow direction in the reactor is periodically reversed, the boundary conditions of the reactor inlet and outlet must also be altered accordingly.

In the application of RFO, the conversion and selectivity were calculated as time-average values, obtained by integration of the actual values over a complete cycle consisting of two flow reversals. Because the outlet concentrations change as function of time, they were also determined by averaging the instantaneous concentration over a complete cycle (Equation 2-10). For the special case of a constant density reactor, the cycle-average conversion can be determined from the cycle-average inlet and outlet concentrations. Similarly, the selectivity and productivity towards N₂, NO, and N₂O were formulated (see definitions in the glossary).

**KINETICS OF AMMONIA OXIDATION**

The selective oxidation of NH₃ on Pt catalyst is an intriguing system for a selectivity study in catalysis and reactor implementation. It demonstrates a relative simplicity and high level of reactivity over an enormous range of experimental conditions. Significant reactivity and selectivity variation have been observed over a temperature range of 423-1773 K and from 1.32 × 10⁻⁷ bar up to 8 bar of the high-pressure process in nitric acid manufacture (Pignet and Schmidt, 1974). The selectivity question is essentially that of the relative yields of NO and N₂. In the lower temperature range (< 573 K), significant production of N₂O might be observed as well, but only trace amounts of this product are observed next to NO and N₂ at higher temperatures. Most of the early work, in particular that of Andrussov (1928) and Bodenstein (1927), laid out over the entire temperature range under mass transfer limiting conditions at higher pressure (1 bar and above). Hence, the dependence of the selectivity on reaction kinetic parameters was unclear.

Low temperature selective oxidation of NH₃ with O₂ to N₂ and H₂O is potentially an efficient method to abate air pollution due to NH₃ (Biermann et al., 1990; Amblard et al., 1999; Gang et al., 2003). Several papers have been published regarding the NH₃ oxidation over Pt/Al₂O₃ catalyst (Ostermaier et al., 1974, 1976) and Pt group metal gauzes (Perez-Ramirez et al., 2004, 2005).
CHAPTER 2. Reactor Modeling, Experimental Set-up, and Steady State Experiments

GLOBAL REACTION

Rate expressions are indispensable in the design of a catalytic reactor, including process start-up and control. Insight into the dependence of the reaction rate on catalyst, temperature, and concentration of reactants, products, and other relevant species is required to predict the reactor dimension and operating conditions. The oxidation of ammonia (NH₃) with oxygen (O₂) may yield the products nitrogen (N₂), nitrous oxide (N₂O), or nitric oxide (NO), according to the exothermic global reactions:

\[ 4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} \quad (2-11) \]
\[ 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \quad (2-12) \]
\[ 4\text{NH}_3 + 4\text{O}_2 \rightarrow 2\text{N}_2\text{O} + 6\text{H}_2\text{O} \quad (2-13) \]

The catalytic oxidation of ammonia is a proper model reaction for the purpose of selectivity manipulation because it involves several parallel reactions. One can obtain nitrous oxide at rather high yield using manganese oxide in the temperature range 573-673 K. Over vanadium pentoxide, ammonia is oxidized to nitrogen at 773-873 K. Nitric oxide is a predominant product over platinum or cobalt oxide in the temperature range 1023-1173 K. All three products can be formed in various ratios, depending on the catalyst type and composition (Dixon and Longfield, 1960). In addition, Il’chenko and Golodets (1975a and 1975b) studied the kinetics of ammonia oxidation over oxides of manganese, cobalt, copper, iron, and vanadium.

In ammonia oxidation, the selectivity problem of the catalytic reaction emerges. This distinguishes ammonia oxidation from the majority of oxidation processes for inorganic substances (H₂, CO, SO₂, HCl, etc.), for which only catalytic activity is essential. At the same time, ammonia oxidation appears to be similar to the selective oxidation of various organic molecules. Since the degree of nitrogen oxidation increases in the sequence of N₂-N₂O-NO, it is natural to consider N₂ to be a mild oxidation product, while N₂O and NO are the products of deep oxidation (Il’chenko and Golodets, 1975a).

ELEMENTARY REACTION STEPS

Catalytic reaction pathways consist of reaction sequences formed by a series of elementary reaction steps. In general, the transient character of a reverse flow reactor implies that steady state kinetics as usually expressed by Langmuir-Hinshelwood type of rate equations cannot be applied. During steady state, rates of adsorption, surface reaction, and desorption are all equal to each other, which is not necessarily the case during transient operation. Moreover, a rate-determining step may vary during a transient, while it is fixed for a
steady state operation. Therefore, the application of a RFR requires that the
reaction kinetics be determined on the level of elementary reaction steps.

The current work uses the ammonia oxidation kinetics as developed by
Rebrov et al. (2002) for Pt/Al₂O₃ catalyst, following work of Bradley et al.
(1997), who observed that adsorbed oxygen, up to coverages of 0.35 ML, does
not block the adsorption of ammonia. The experimentally obtained kinetic
results were interpreted with a dual site mechanism. This means that
nitrogen-containing species occupy one type of sites, so-called top sites, while
non-nitrogen containing species occupy another type, known as hollow sites.
An exception is that adsorbed N itself can be considered in the hollow sites
instead of top sites. According to experimental results on ammonia synthesis
over Ru, adsorbed N residing in hollow sites was energetically favoured
(Zhang et al., 2002). The elementary steps of the kinetic scheme and the
reaction rate parameters are shown in Tables 2-2 and 2-3, respectively.

Some values of the kinetic model parameters as developed by Rebrov et al.
(2002) were slightly adapted to provide accurate predictions for own
experimental steady state data (to be discussed following page 37) with
respect to NH₃ and O₂ conversions, as well as the selectivities to N₂, NO, and
N₂O. This is reasonable because the current catalyst, although Pt/Al₂O₃ as
used by Rebrov et al. (2002), is not exactly the same. The platinum loading and
the number of surface sites (obtained from CO chemisorption) were different
(see Table 2-4). Moreover, the residence time of the gas in the reactors used
was completely different as well. It is emphasized that the activation energies,
reported here, only show minor differences from the values reported by
Rebrov et al. (2002). A comparison of experimental data and model
predictions starts on page 37.

SOFTWARE DEVELOPMENT

The software development aims to simulate a reverse flow reactor for
ammonia oxidation. The simulations were performed for reasons as follows:

- To demonstrate that the principle of RFO may improve the performance of a
  fixed bed reactor when it is compared to steady state operation. The accuracy
  of the kinetic model is of minor importance with respect to this target.
- To explore the possible range of experimental conditions, where benefits from
  reverse flow operation can be expected.
- To obtain a better insight in the required technical scale of operation during
  laboratory experiments.
The dynamic behaviour of the reactor operation under periodic flow reversal is characterized by a moving reaction front, accompanied by possibly steep gradients in either concentrations or temperatures. When a fixed grid is used for spatial discretisation, the change of the numerical solution at each point may be very fast, which by consequence demands very small time steps and a very large number of mesh-points. A lot of efforts have been put lately in the development of adaptive grid methods to handle moving steep gradients. Although a few fixed grid methods present good characteristics, a moving grid method may be used more efficiently by refining the grid only around steep gradients whenever found. Most of the studies presented in the literature on the simulation of reactors under periodic flow reversal utilize the methods proposed by Eigenberger and Nieken (1988) to adapt the grid to the solution, using a modified Crank-Nicholsan technique with automatic space grid adjustment. The method is potentially time saving because it uses a comparatively low number of grid points.
Table 2-3. Reaction rate parameters concerning the elementary steps in Table 2-2. Adapted reaction rate parameters in comparison to Rebrov et al. (2002) are shown in the right section. They refer to own steady state experiments. Pre-exponential factors are in $\text{s}^{-1} \text{atm}^{-1}$ and $\text{s}^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>$r_k$</th>
<th>$A$</th>
<th>$E_a$</th>
<th>$\phi$</th>
<th></th>
<th>$r_k$</th>
<th>$A$</th>
<th>$E_a$</th>
<th>$\phi$</th>
</tr>
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<tbody>
<tr>
<td>1a</td>
<td>2.00x10^8</td>
<td>0.0</td>
<td>0.0</td>
<td>1a</td>
<td>2b</td>
<td>6.04x10^15</td>
<td>9.60x10^4</td>
<td>0.0</td>
<td>2b</td>
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<tr>
<td>3a</td>
<td>4.30x10^6</td>
<td>0.0</td>
<td>0.0</td>
<td>3a</td>
<td>4b</td>
<td>1.00x10^13</td>
<td>2.13x10^5</td>
<td>6x10^4</td>
<td>4b</td>
</tr>
<tr>
<td>5b</td>
<td>1.14x10^14</td>
<td>1.31x10^5</td>
<td>0.0</td>
<td>5b</td>
<td>1.25x10^10</td>
<td>8.76x10^4</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td>2.10x10^11</td>
<td>9.82x10^4</td>
<td>0.0</td>
<td>6b</td>
<td>1.00x10^11</td>
<td>9.70x10^4</td>
<td></td>
<td></td>
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<td>7b</td>
<td>4.10x10^9</td>
<td>8.60x10^4</td>
<td>0.0</td>
<td>7b</td>
<td>1.31x10^17</td>
<td>1.70x10^5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8b</td>
<td>1.00x10^13</td>
<td>1.18x10^5</td>
<td>0.0</td>
<td>8b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9b</td>
<td>1.00x10^11</td>
<td>4.82x10^4</td>
<td>0.0</td>
<td>9b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10b</td>
<td>5.65x10^12</td>
<td>1.21x10^5</td>
<td>0.0</td>
<td>10b</td>
<td></td>
<td></td>
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<tr>
<td>11a</td>
<td>2.00x10^8</td>
<td>6.05x10^4</td>
<td>0.0</td>
<td>11a</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>12b</td>
<td>1.00x10^13</td>
<td>1.40x10^5</td>
<td>0.0</td>
<td>12b</td>
<td>1.19x10^5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13a</td>
<td>2.50x10^8</td>
<td>7.22x10^4</td>
<td>0.0</td>
<td>13a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The flow reversals induce time dependence, while the fluid flow through the reactor bed creates axial profiles. Such conditions lead to partial differential equations and the complexity of the reactor model. Therefore, the model equations suitable for RFO must be solved numerically. In this work, the software package FlexPDE (PDE Solutions Inc., 2001, 2004) was used to solve Partial Differential Equation (PDE’s), coupled with Ordinary Differential Equations (ODE’s) and algebraic equations. Each continuity equation in the gas phase gave rise to a PDE (see Equation 2-1), while each surface species led to an ODE (see Equation 2-2). Vacant top and hollow sites were written, each as an algebraic equation (see Equations 2-3 and 2-4) in order to reduce the complexity during the numerical calculations.

FlexPDE is a scripted finite element model builder and numerical solver (Backstrom, 1999). It means that from a script written by the user, FlexPDE performs the operations necessary to turn a PDE system into a finite element
model and solve the system of equations. The FlexPDE calculations also involve automatic remeshing when stiff profiles prevail. Such events may happen in particular due to discontinuities when the flow direction is periodically reversed.

EXPERIMENTAL SET-UP

In order to obtain transient data during RFO, a dedicated experimental set-up of a reverse flow reactor and online analysis are required. The reverse flow reactor used in this work is a small-scale laboratory reactor. Transient data are obtained while alternating the flow direction. With the same set-up, steady state data can also be obtained by operating the reactor in unidirectional flow.

The classical application of reverse flow, aiming at maximum energy saving, strives for a full adiabatic temperature rise in the reactor. By consequence the reactor diameter should be relatively large as to avoid heat losses to the environment. In the application for selectivity manipulation as in the current work, the aspect of adiabatic operation seems less crucial, which would mean that a much smaller laboratory reactor could be applied. Focus was on the assessment of intrinsic kinetics and the subsequent study on how to apply those kinetics to see if RFO provides advantages. Therefore, it is not desired to disguise the kinetics by additional features like temperature and concentration gradients that might arise from mass or heat transfer limitation. Moreover, a plug flow pattern is desired as mixing causes a loss of kinetic influences. Pressure drop causes density and concentration changes, which again weaken the influence of kinetics. Various well-known literature criteria to avoid pressure drop over the fixed bed reactor, axial and radial dispersions, and heat and mass transfer limitations were considered in the fixed bed reactor design (Mears, 1971; Froment and Bisschoff, 1990; Dautzenberg, 1994) in order to assess the kinetic regime. One should realize that heat and mass transfer limitations might be present in an industrial application. However, selectivity usually remains governed by kinetics.

SCHEMATIC VIEW OF EXPERIMENTAL SET-UP

A schematic view of the experimental set-up and its picture are outlined in Figures 2-3a and 2-3b, respectively. The set-up basically consists of a feed section, a reactor section, and an online gas analysis section. This set-up was designed with a fully automated control system. The experimental set-up is run from a computer, which is friendly programmed to operate and to control the reactor. This computer is equipped with data-acquisition cards to allow data collection. Since the set-up was computerized, opening and closing all solenoid valves at very short switching times can be perfectly incorporated.
Moreover, the flow rates of the inlet gases, which determine the composition of the reactor feed can be precisely set with Brooks’ mass flow controllers. A back-pressure controller was installed in order to avoid pressure changes in the reactor due to sudden switching, while for safety reasons, a pressure relief valve was present. Downstream the reactor just before the vent, a water condenser was installed to avoid condensation of the reaction product water in the vent system. Safe operation was invoked by the presence of leakage gas detectors and several alarm sensors, to warn for emergency situations. A primary shut down key was equipped as a safe barricade in the case that failures cannot be handled.

The control system consisted of one rack with one communication module and various types of I/O modules. All digital I/O were performed via a digital PCI card (National Instrument) inside the computer. Labview software runs the computer, which is connected to the Fieldpoint communication module. Labview takes care of all data-acquisition and control actions.

**Feed gas section**

The feed section consists of six different gas lines, viz. \( \text{NH}_3, \text{O}_2, \text{N}_2, \text{NO}, \text{N}_2\text{O}, \) and \( \text{He} \). Each line contains a pressure reducer, open/close valve, one-way valve, and a mass flow controller. Each gas can be supplied separately or in a mixture for calibration purposes. \( \text{NH}_3, \text{O}_2, \) and \( \text{He} \) mixtures are used as reactor feed during both steady state and reverse flow experiments. A static mixer (M-101, Figure 2-3a) provides blending before entering the reactor.

**Reactor section**

The reactor section consists of preheaters (in-line resistance heating of each feed), a stainless steel fixed bed reactor, and a heated line behind the reactor. The preheaters provide the desired inlet temperature; the heated outlet line prevents water condensation. The reactor is contained in a fluidized sand bath to heat the reactor during the start-up and to maintain isothermal conditions during experiments. Typical reactor data are given in Table 2-4.

The feed section ends up in two separate lines, one for each reactor inlet. The reactor ends can act as an inlet or an outlet, depending on the flow direction. A cross section of the reactor is depicted in Figure 2-4. The reactor is loaded with catalyst \( \text{Pt}/\text{Al}_2\text{O}_3 \) retained by two sintered quartz plates. Sample chambers at both sides of the catalyst bed are connected via capillaries to the online mass spectrometer for real time analysis. A thermocouple tube allows monitoring the axial temperature profile along the catalyst bed. The total pressure in the reactor is kept constant at 1 bar and \( \text{He} \) is used as bulk gas.
CHAPTER 2. Reactor Modeling, Experimental Set-up, and Steady State Experiments

Figure 2.3a. Schematic view of the experimental set-up consisting of feed gas section (left), reactor section (upper right), and analysis section (lower right).
Most crucial are the four-switching valves, which direct one feed to the reactor and stop the other feed. The valves are placed just behind the feed splitting point and in front of the feed gas preheater to avoid heat damage. The valves are alternately operated (two valves open, two valves closed), depending on the flow direction. For the reactor feed line where the valve is open, the feed gas passes a short of check valve, consisting of a sapphire bead and spring release, before it enters into the catalyst bed. A similar check valve is placed in the reactor outlet. To prevent gas outflow via the wrong outlet, a high pressure of helium is operated on that outlet to keep the sapphire bead in a close position. When the flow direction needs to change, the antipode situation holds.

**Analysis section**

The analysis section consists of an online mass spectrometer (VG Sensorlab 200D) both for steady state and transient measurements. The mass
spectrumeter measures \( \text{NH}_3 \) (m/e = 17), \( \text{O}_2 \) (m/e = 32), \( \text{N}_2 \) (m/e = 28), \( \text{NO} \) (m/e = 30), \( \text{N}_2\text{O} \) (m/e = 44), \( \text{H}_2\text{O} \) (m/e = 18), and \( \text{He} \) (m/e = 4) concentrations. Both the reactor inlet and outlet can be analyzed. Analysis of the gas sampling can be performed with a frequency of \( 120/n \) Hz, where \( n \) is the number of masses analyzed. Daily calibration of the mass spectrometer is required for obtaining quantitative data from the experiment. Detailed information about this mass spectrometer system, which is appropriate for the transient kinetic experiments, has been reported (Campman, 1996; Nievergeld, 1998; and Harmsen, 2001).

When reversing the flow direction of the feed, the sampling points to measure the product concentration need to switch. It is performed by using a 4-way sample valve, which allows the outlet gas sample to flow into the mass spectrometer, while the other one is flushed before being used for subsequent sampling. This valve works with the same frequency as the switching valves for reversing the flow direction, although some delay time could be installed. If desired, the sampling point can be fixed at one end of the reactor without switching the 4-way sample valve. In this condition, the mass spectrometer measures the inlet during one half-cycle and the outlet during the other half cycle. The PC-1 is used to monitor the online gas analysis and the PC-2 is used to operate and control the processes (see Figure 2-3a). The PC-2 controls all valves that are automatically operated.

**EXPERIMENTAL PROCEDURE**

The experimental procedure for the selective oxidation of \( \text{NH}_3 \) can be described as follows, see Figure 2-3a. Firstly, the water condenser (C-101) for cooling down the off-gas starts running. The reactor (R-101) is heated via the fluidized sand bath heater to the desired reaction temperature, while \( \text{He} \) (TP-07) flows through in one direction. Ammonia (TP-01) at certain concentration is introduced into the reactor when the reactor temperature has been reached, subsequently followed by \( \text{O}_2 \) (TP-06). The feed compositions can be set from the mass flow controllers (FIC-011 for \( \text{NH}_3 \), FIC-061 for \( \text{O}_2 \)). Before entering the reactor, the feed gas mixture is blended in a static mixture (M-101). The preheaters (shown in traced line in front of the reactor) are installed near the reactor to gain the desired inlet temperature, which is approximately close to the reaction temperature. The reaction products are continuously measured with the mass spectrometer. When the reactor attains steady state, which is indicated by the observed outlet concentrations, experiments under flow reversal can start. The flow direction is periodically reversed at every switching time, automatically induced by the computer (PC-2), using valves XV-103 and XV-102 for the inlets, XV-081 and XV-082 for the outlets. When the reactor stands by after completion of the daily experiments, a low \( \text{He} \) flow rate is maintained at a temperature of 373 K.
All experiments were carried out under conditions for intrinsic chemical kinetics when judged with well-known criteria, which were developed for steady state kinetic research (Mears, 1971a, 1971b; Rosendall and Finlayson, 1995). For the majority of data, the intrinsicity will not be affected by the applied transients (Hoebink et al., 1999), although this cannot be guaranteed shortly after switching the flow direction. Ammonia oxidation over alumina-supported platinum catalyst does not occur at temperatures below 473 K (Ostermaier et al., 1974, 1976). This is the reason to carry out the experiment in this study at distinct higher temperatures. The oxidation of ammonia in oxygen excess was studied in detail at temperatures below 653 K. In this case, it was reported by Sadykov et al. (2000) that there was no mass transfer limitation.

**CATALYST**

The catalyst 0.05% Pt/γ-Al₂O₃ support as used in this work was provided by Unicore A.G. (Hanau). The catalyst particle was crushed and sieved to obtain a pellet size that minimizes the influence of intra particle diffusion. The catalyst was analyzed via CO chemisorption. Catalyst data, reactor specification, and typical operating conditions during the steady state and reverse flow experiments are shown in Table 2-4, unless otherwise indicated.

**Table 2-4. Catalyst, reactor properties, and operating conditions.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total reactor length (m)</td>
<td>30 × 10⁻³</td>
</tr>
<tr>
<td>Inner reactor diameter (m)</td>
<td>15 × 10⁻³</td>
</tr>
<tr>
<td>Catalyst mass loaded (kg)</td>
<td>3.5 × 10⁻³</td>
</tr>
<tr>
<td>Pt loading (%)</td>
<td>0.05</td>
</tr>
<tr>
<td>Capacity of catalyst (molsites kg⁻¹cat)</td>
<td>2.86 × 10⁻⁶</td>
</tr>
<tr>
<td>Metal dispersion (%)</td>
<td>50</td>
</tr>
<tr>
<td>Metal surface area (m² kg⁻¹cat)</td>
<td>62</td>
</tr>
<tr>
<td>Catalyst pellet diameter (m)</td>
<td>1.06-2.12 × 10⁻⁴</td>
</tr>
<tr>
<td>Specific surface area (m² g⁻¹)</td>
<td>93</td>
</tr>
<tr>
<td>Pore volume (BET, cm³ g⁻¹)</td>
<td>0.35</td>
</tr>
<tr>
<td>Catalyst pellet density (kg m⁻³)</td>
<td>1230</td>
</tr>
<tr>
<td>Catalyst bulk density (kg_cat m⁻³)</td>
<td>722</td>
</tr>
<tr>
<td>Bed porosity (m³_g m⁻³)</td>
<td>0.40</td>
</tr>
<tr>
<td>Switching time $t_s$ (s)</td>
<td>2 – 30</td>
</tr>
<tr>
<td>Total pressure (bar)</td>
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</tr>
<tr>
<td>Temperature (K)</td>
<td>523 – 673</td>
</tr>
<tr>
<td>Residence time $\tau$ (s)</td>
<td>0.3 – 0.9</td>
</tr>
<tr>
<td>NH₃ in feed (mol %)</td>
<td>1</td>
</tr>
<tr>
<td>O₂ / NH₃ ratio in feed</td>
<td>1 - 3</td>
</tr>
</tbody>
</table>
CHAPTER 2. Reactor Modeling, Experimental Set-up, and Steady State Experiments

PRE-EXPERIMENTS

CATALYST PRETREATMENT

A fresh catalyst bed is heated under He flow by ramping the fluid bed temperature and the feed gas temperature at a rate of about 10 K per minute from room temperature to 773 K, which is 100 K higher than the maximum temperature planned for experiments. The catalyst is then gently oxidized by a stream containing 1 vol.% O\textsubscript{2} in He, while the temperature during the catalyst pretreatment is maintained constant. The catalyst oxidation goes on for about 3 hours. Then the O\textsubscript{2} flow is stopped, and the catalyst is kept under flowing He for about half an hour in order to purge reversibly adsorbed oxygen and other residual components. Finally, the catalyst is reduced with a 1 vol.% of H\textsubscript{2} in He flow for 1 hour. The reactor is eventually allowed to cool down under He flow to the desired temperature of planned experiments by adjusting the feed gas temperature and the fluidized bed temperature. Particular attention must be paid to flush all H\textsubscript{2} contained in all possible lines after the catalyst pre-treatment. More details about the catalyst pretreatment have been reported elsewhere (Campman, 1996).

LINE-OUT PROCEDURE

It was found from introductory experiments that the catalyst exhibited a higher initial activity after daily start-up as compared to its activity after more than 3 hours on-stream. Significant deactivation during NH\textsubscript{3} oxidation over alumina-supported platinum catalyst was already reported in the literature (Ostermaier et al., 1974, 1976) and is due to catalyst saturation with reacting species. Therefore, a line-out procedure had to be carried out in order to minimize the influence of the reversible start-up effects on experimental results. Figure 2-5 shows the decay of the NH\textsubscript{3} conversion as function of time-on-stream after storage of the catalyst in a He stream. A profound decay takes place in about 3 hours, and afterwards the conversion remains fairly stable.

DETERMINATION OF RESIDENCE TIME AND BED POROSITY

In practice, bed porosity is often assumed uniform along the reactor. One should realize, however, that the actual bed porosity of the fixed bed reactor is difficult to measure if the catalyst pellets are porous. A novel method for the determination of bed porosity is proposed. This method is developed by a
combination of reverse flow operation and lowering the feed concentration just before the flow is reversed.

![Figure 2-5](image)

Relative ammonia conversion as a function of time-on-stream after catalyst storage in 5000 nml He/h at 373 K. Conditions: \( T = 573 \) K, \( \text{NH}_3 = 1 \text{ vol.\%} \), \( \text{O}_2 = 5 \text{ vol.\%} \), balance He. Total flow rate 10.000 nml/h.

The execution of the experiment for determining the residence time and bed porosity is as follows. The feed gas consisting of two non-reacting components (argon in helium) flows through the horizontal reactor from the left to the right at certain volumetric rate and feed composition. The concentration of the inlet gas is measured via online mass spectrometry. The position of gas sampling is fixed at the left hand side of the reactor. This feed composition flows through the reactor for \( t_H \) seconds, i.e. time period, in which argon is at high concentration, and subsequently for \( t_L \) seconds, i.e. time period in which argon is at low concentration. So \( t_H + t_L \) equals the switching time \( t_s \). This scheme repeats when the flow direction is reversed from right to the left (see Figure 2-6). The total volumetric rate during the high and low concentrations of argon remains constant by adjusting the helium flow rate. The mass spectrometer measurement at the fixed point indicates the difference of time period between the right and left directions. The time difference is induced by the fact that the reactor gas hold-up with low concentration of argon is measured again when the flow direction is from right to left. The front gas composition from right to left at high argon concentration will be measured with the mass spectrometer with a delay time of \( \tau_o \) seconds after switching the flow direction, while one reactor hold-up with low concentration of argon moving from right to left will not reach the sampling point since the flow direction is changed again from left to right. This time difference can be expressed in Equation 2-18:

\[
\begin{align*}
t_H + t_L + \tau_o &= t_s + \tau_o \quad \text{first measured time period} \\
t_H + t_L - \tau_o &= t_s - \tau_o \quad \text{second measured time period}
\end{align*}
\]
Once the gas residence time has been determined, the effective bed porosity can be calculated as:

\[ \varepsilon_b = \tau_0 \frac{F}{V_r} \]  

\[ (2-19) \]

**Figure 2-6.** Determination of residence time by combining reverse flow operation and feed concentration steps for Ar in He flow.

**STEADY STATE EXPERIMENTS**

Steady state experiments were carried out to assess the reaction kinetics. Moreover, these data are used as a basis to judge the potential of reverse flow operation procedures. Experimental data are compared to model predictions as explained on page 25.

**EFFECT OF REACTION TEMPERATURE**

**Figure 2-7** shows the effect of reaction temperature on the conversion and selectivities during the steady state experiments for O₂ to NH₃ feed ratios of 1:1 (Figure 2-7a), 2:1 (Figure 2-7b), and 3:1 (Figure 2-7c). Increasing the reaction temperature gives rise to an increase of the ammonia conversion at all oxygen concentrations. The trend of conversion increase is in a good agreement with various literature data: for instance, Gang et al. (2003). The selectivities to N₂, NO, and N₂O exhibit different behaviour when increasing the temperature. At relatively low temperature, N₂ is the main reaction product, followed by N₂O, while NO is hardly detected (Ill'chenko and Golodets, 1975b). This is in a good agreement with the experimental results as shown in **Figure 2-7**. At higher temperature, the selectivity to N₂ shows a slight decrease, while the selectivity to N₂O passes through a maximum. The selectivity to NO increases with increasing temperature.
In Figure 2-7, the selectivity to $N_2$ tends to decrease with increasing reaction temperature. A higher reaction temperature induces an abundance of the oxygen surface coverage leading to deep oxidation products ($N_2O$ or NO). However, the selectivity to $N_2O$ decreases when the temperature rises further. The decomposition of $N_2O$ over platinum catalyst occurs at substantially higher temperature than ammonia oxidation (II’chenko and Golodets, 1975a). As a result, the selectivity to NO continues to rise.

At even higher temperature, NO dominates among the reaction products as might be foreseen from an extrapolation of Figure 2-7, in particular at high $O_2$ to $NH_3$ feed ratios. The selectivity towards NO attains high values when oxygen coverage on the catalyst surface is high. It was reported by Sadykov et al. (2000) that there was almost no $NH_3$ or its partial oxidation products on the surface. This statement was checked by computer simulation, which results in a good agreement.

\[\text{Figure 2-7.}\]
Conversion of $NH_3$ and selectivities to $N_2$, NO, and $N_2O$ as a function of temperature. Feed ratios of $O_2$ to $NH_3$ are 1:1 (a), 2:1 (b), and 3:1 (c). Residence time is 0.6 s. Data points refer to experiments, curves to model predictions with the kinetic scheme of Tables 2-2 and 2-3.
The coverage of the adsorbed components on the catalyst surface was simulated at 573 K and 673 K. The profiles of adsorbed components along the reactor length were more pronounced at 573 K than at 673 K (see Figures 2-8a and b). The level of oxygen coverage slightly decreases at higher temperature due to a slightly higher consumption rate for the conversion of NH$_3$ and notably other surface reactions consuming adsorbed oxygen. Accordingly the number of vacant top sites and hollow sites is larger at higher temperature.

The curves in Figure 2-7 represent predictions of conversion and selectivity as provided by the kinetic model of Rebrov et al. (2002) as shown in Table 2-2 with minor adaptation of the rate parameters (Table 2-3). In general, there is a good agreement between model predictions and experimental data. The model underestimates the conversion at 523 K. It is known that the reaction does not proceed at 473 K over Pt/Al$_2$O$_3$ (Ostermaier et al., 1974, 1976). On the higher temperature side, the model predicts a slight increase of the selectivity to N$_2$, which is not confirmed by the experiments. One could expect that mass transport effects may become more important at higher temperatures.

**Figure 2-8.**
Model prediction of adsorbed components on the catalyst surface along the reactor axis. Feed ratio of O$_2$ to NH$_3$ is 3:1. Residence time is 0.6 s. Temperature is 573 K (a) and 673 (b).

**EFFECT OF OXYGEN CONCENTRATION**

The oxygen concentration in the feed plays an important role for the conversion of ammonia and selectivity towards the products. Figure 2-9 shows the influence of oxygen concentration on conversion and selectivity. The model predictions are in good agreement with the experimental data at 573 K, while at 623 K the model underestimates the selectivity towards N$_2$ and overestimates the selectivity towards N$_2$O at high oxygen content. It was
observed during the experiments that a higher oxygen concentration gives rise to a slight increase of ammonia conversion. More oxygen in the feed provides more adsorbed oxygen on the catalyst surface, as apparently the productions of NO and N₂O are favoured while suppressing the selectivity to N₂ (Figure 2-9). The slightly higher oxygen coverage can be seen from Figure 2-8a (O₂: NH₃ = 3:1) in comparison to Figure 2-10 (O₂: NH₃ = 1:1).

**Figure 2-9.**
Conversion of NH₃ and selectivities towards N₂, NO, and N₂O as a function of oxygen concentration at T = 573 K (a) and 623 K (b). The residence time is 0.6 s. Data points refer to experiments, curves to model predictions with the kinetic scheme of Tables 2-2 and 2-3.

In general, increasing the oxygen concentration in the feed gives rise to a decrease of the selectivity to N₂, while the selectivities to N₂O and NO increase (see Figure 2-9), which behaviour is in accordance with many literature data.
The selectivity to N₂O shows a decrease after reaching a maximum value. This decrease might be induced by the decomposition of N₂O into N₂. The maximum depends on temperature and oxygen concentration. At 3 vol.% oxygen in the feed, the maximum is at slightly lower temperature (573 K) than at 1 vol.% oxygen (623 K), see Figure 2-7.

**EFFECT OF RESIDENCE TIME**

An increase of the selectivity towards N₂ at high temperatures has been ascribed to parallel and consecutive reactions or reductions with NH₃ (Il’chenko and Golodets, 1975b), and decomposition reactions (Il’chenko and Golodets, 1975a; Pignet and Schmidt, 1974). A net competition between NO production and decomposition or consecutive reactions might occur. The oxidation of N₂ to N₂O is impossible thermodynamically. Equations 2-20 to 2-24 give an overview of possible decomposition and consecutive reactions. About these side processes, which affect the process selectivity, there is no agreement in the literature. Most researchers believe that NO decomposition to N₂ and O₂, and ammonia interaction with nitrogen oxide yielding N₂ and water, provide the largest contribution (Perez-Ramirez et al., 2005). Although the NO decomposition is thermodynamically favourable (ΔG° = -86 kJ mol⁻¹), its activation energy is very high (364 kJ mol⁻¹) (Fritz and Pitchon, 1997).

\[
\begin{align*}
2NH_3 + 3N_2O & \rightarrow 4N_2 + 3H_2O \quad (2-20) \\
2NH_3 + 3NO & \rightarrow 2.5N_2 + 3H_2O \quad (2-21) \\
N_2O & \rightarrow N_2 + 0.5O_2 \quad (2-22) \\
2NO & \rightarrow N_2 + O_2 \quad (2-23) \\
2N_2O & \rightarrow N_2 + 2NO \quad (2-24)
\end{align*}
\]

According to data obtained by Kuchaev and Temkin (1988), there are two distinct kinetic regions for ammonia consumption. In the first region, the reaction rate is proportional to the ammonia partial pressure (first order with respect to ammonia) and does not depend on the oxygen content (zero order with respect to oxygen). In the second region, the reaction rate is proportional to the oxygen partial pressure and does not depend on the ammonia content.

If the scheme of the consecutive decomposition of N₂O and NO is true, the observed N₂O and NO formations should decrease, while the rate of N₂ formation should increase with increasing residence time. If NH₃ oxidation to N₂, NO, and N₂O occurs without subsequent decomposition, the rates and selectivities should not depend on the residence time.
Figure 2-11 demonstrates the relation between the conversion of \( \text{NH}_3 \) and the selectivities to \( \text{N}_2 \), \( \text{NO} \), and \( \text{N}_2\text{O} \) versus the residence time. The conversion of \( \text{NH}_3 \) should increase if the reaction occurs at longer residence time. The experimental results show a slight increase of conversion as the conversion of \( \text{NH}_3 \) has already reached a high level. The model can not predict quite well the \( \text{NH}_3 \) conversion at short residence time. The selectivities to \( \text{N}_2 \) and \( \text{NO} \) tend to increase slightly when the residence time increases, while the selectivity to \( \text{N}_2\text{O} \) decreases a little. These observations show the oxidation of ammonia proceeds via oxidation reactions as well as consecutive and decomposition reactions. This scheme is in a good agreement with the results of Sadykov et al. (2000), who state that with increasing contact time, the nitrous oxide yield decreases, but this is explained by \( \text{N}_2\text{O} \) interaction with ammonia on the catalyst surface. NO yield passes through a maximum at a definite gas flow rate or respective contact time as reported by Atroshenko and Kargin (in Sadykov et al., 2000). The usual explanation is that nitrogen oxide is unstable and decomposes at long contact times. However, Apelbaum and Temkin (in Sadykov et al., 2000) proved that decomposition of NO does not occur under the usual operation conditions of ammonia oxidation because excess oxygen suppresses this reaction. According to estimations by Beskov et al. (in Sadykov et al., 2000), the decomposition of NO into \( \text{N}_2 \) and \( \text{O}_2 \) is only 2-3 orders of magnitude lower than the reaction rate of ammonia oxidation to produce NO and \( \text{H}_2\text{O} \).

**CONCLUDING REMARKS**

In this chapter, a glossary of definitions and terminologies was given as used throughout this thesis. The mathematical model of a RFR was presented including the boundary and initial conditions. A brief discussion about the
software package FlexPDE was made as the model was solved with this package. Because the main goal of the project is not to develop the kinetic scheme, a kinetic model for the selective oxidation of NH₃ was taken from the literature. Steady state experiments were performed in order to validate the kinetic model. Some rate parameters, compared to the literature data, had to be slightly adapted. In general the elementary step model seems adequate to describe the experimental data, meaning that it can be applied to describe reverse flow experiments.
Chapter 3

Reverse Flow Operation

A single conversation with a wise man is better than ten years of study

§ Introduction
§ Analysis of reverse flow reactor behaviour
§ Simulation of reverse flow reactor
§ Experiments
§ Results and discussion
§ Concluding remarks

Summary
In principle, reactor perturbation by flow reversal can be implemented for manipulation of catalyst surface coverage if a dedicated and proper operation procedure can be developed. A mathematical model and analysis of reverse flow reactor behaviour for the ammonia oxidation on platinum start the discussion. Series of reverse flow experiments were carried out on a laboratory reactor scale. The influence of flow reversals on the conversion and selectivity at various switching times was observed and evaluated. Other process variables such as gas residence time, reaction temperature, and oxygen concentration in the feed were points of interest. Assessment of reactor dynamics can be achieved most expediently by implementing a comparable switching time and gas residence time. Model and experimental results indicate that regular reverse flow operation for manipulation of catalyst surface coverage always induces a decrease of conversion. It was also found that the selectivity due to flow reversal was rather insensitive to changes in the switching frequency.
CHAPTER 3. Reverse Flow Operation

Reverse flow operation (RFO) is primarily an engineering technique for energy trapping inside a reactor. A large literature body concerning this technique has been developed over the 30 years since periodic operation was first proposed. In its development, various applications and achievements have been made. Many items on RFO, nevertheless, are still unknown or even untouched.

This study aims at manipulation of catalyst surface coverage in the reactor by adopting the concept of reactor perturbation through flow reversal. The peculiarity of this application is forcing a reaction system to proceed under transient rather than steady state conditions with the objective to largely improve conversion and/or selectivity compared to steady state operation. All measured variables become time dependent under this type of operation, and performance should be judged on a time-average basis.

In Chapter 2, the ammonia oxidation at steady state, once-through operation (SSO) has been discussed. As noted earlier, these experiments were necessary to judge the potential of reverse flow operation, with steady state operation as a basis for comparison. In Chapter 3, the application of regular RFO for selective oxidation of ammonia will be discussed. Regular RFO stands for reverse flow without the special features that are addressed in Chapter 4 and Chapter 5.

INTRODUCTION

In most RFO cases, the catalyst acts not only as a chemical reaction booster, but also as a heat sink necessary for accumulating energy from the exothermic reaction due to the fact that the heat capacity of the catalyst bed is much higher compared to that of the processed gas. In this respect, the catalyst bed eventually provides a periodic heat exchange between the stored energy and the cooler feed gas (Matros and Bunimovich, 1996). One of the proposed methods consists of periodic gas flow reversals in a fixed catalyst bed to maintain a slowly moving front of heat and chemical reaction. Such a front is formed when the inlet gas with low temperature is fed into a previously heated bed (Padberg and Wicke, 1967). An important characteristic of RFO is that substantial non-steady concentration and temperature fields are induced in a catalyst bed (Matros, 1989).

Further applications on coupling between exothermic and endothermic reactions are indeed interesting. Kulkarni and Dudukovic (1996) studied mixing of the endothermic and exothermic reactants, as designated by a direct coupling. This system can eliminate the need for a heat exchanger. It can also avoid catalyst deactivation. Indirect coupling an endothermic reaction (steam reforming) and an exothermic reaction (hydrocarbon combustion) has been
simulated by Kulkarni and Dudukovic (1996, 1997). Another application of RFR for highly endothermic heterogeneously catalyzed gas phase reactions at high temperatures with rapid, but reversibly catalyst deactivation was studied by van Sint Annaland et al. (2002a, 2002b).

Periodic flow reversals provide a way to affect the surface coverage of catalytic sites. In the case of non-linear kinetics, changes in conversion or selectivity could be substantially expected when compared to once-through operation (Budhi et al., 2003b, 2004a). If the catalyst is operated under unsteady-state conditions, it is therefore possible to attain such a state, gas composition, and structure that would allow a noticeable increase in the selectivity and the productivity of a process. Unsteady-state operation allows the processing of reaction gases with both constant and varying inlet parameters (Boreskov and Matros, 1983). Reverse flow operation might permit higher conversion than steady state operation in a single catalyst bed. For the experiments of SO$_2$ oxidation or ammonia synthesis, cycle-average conversions under unsteady state conditions were reported around 5% higher than for steady state (Boreskov et al., 1982; Boreskov and Matros, 1983).

The performance of a fixed-bed reactor with periodic flow reversal is dependent on design parameters, such as reactor length and overall bed porosity, as well as operating parameters, such as feed concentration, gas flow rate, and flow switching frequency (Salinger and Eigenberger, 1996). In this study, the experimental investigation of a laboratory scale reactor in reverse flow mode is presented for the selective oxidation of ammonia into either nitrogen, nitric oxide, or nitrous oxide. The primary goal is to demonstrate that reverse flow operation may create dynamic changes of active site coverages, which might yield a conversion and selectivity that differ from the steady state, once-through operation. Apart from the three process variables: temperature, residence time, and feed oxygen concentration, that characterize the steady state, one needs a new parameter $\alpha$, defined as the ratio of the switching time and the gas residence time in once-through operation in order to clearly define reverse flow operation conditions.

**ANALYSIS OF REVERSE FLOW REACTOR BEHAVIOUR**

**SWITCHING TIME**

The cycle time in the classical application of RFO for energy saving, defined as the time required for a heat wave to pass through the bed, is typically of the order of several minutes for high-pressure processes to several dozens of minutes for SO$_2$ oxidation. If the reaction steps or side processes defining the
catalyst state dynamics occur on a time scale comparable with the cycle duration, then the catalyst state will be non-steady (Bunimovich et al., 1995).

In the application of a reverse flow reactor for energy saving, it is important to know the dependence of the maximum bed temperature on the operating conditions and kinetic parameters to prevent catalyst deactivation and undesirable side reactions. Nieken et al. (1995) found that the maximum temperature was rather insensitive to changes in the switching frequency when a first-order, irreversible reaction occurred in a reactor without inert section. Two limiting cases were considered, i.e. very low and very high flow reversal frequency. In the case of a low switching frequency, the temperature front moves downstream at a constant shape and velocity. This behaviour was first studied by Wicke and Vortmeyer (1959). In the high switching frequency case, first considered by Matros (1989), the solid temperature profile remains essentially stationary due to the very high heat capacity of the solids relative to that of the gas. When the switching frequency is very low, the reactions may be completed either in a temperature front moving at a constant velocity and shape, or in two consecutive temperature fronts separated by an almost constant temperature plateau with the upper front moving faster than the lower one (Somani et al., 1997).

The time scale of flow reversals in a fixed bed reactor with an imposed temperature profile, necessary for manipulation of the selectivity, appears in the order of seconds, which is significantly smaller than the order of minutes, used in the classical reverse flow application for energy saving (Budhi et al., 2003b, 2004a). A first estimate of the time scale can be obtained from the ratio of the storage capacity of the catalyst and the feed flow rate of the reactant. It means that manipulation of the reactor selectivity requires considerably more frequent flow reversals in order to keep the catalyst surface in a dynamic state. If the reaction rate is fast compared to reversing the flow direction, then there is essentially a steady-state present for the reaction rate and corresponding catalyst surface coverages. If an antipode situation exists, then real unsteady-state behaviour holds for the system.

**AVERAGE RESIDENCE TIME**

In once-through operation, the residence time \( \tau_0 \) is defined as the time required to process one reactor volume of feed measured at specified conditions. The definition of residence time could be different in the case of RFO as flow reversals affect the trajectory of a fluid element through the reactor. The gas residence time in the case of RFO depends on the parameter \( \alpha \). If the switching time is larger than the gas residence time \( (\alpha > 1) \), the leading gas has the residence time as defined in once-through operation. The part of the gas that cannot pass the bed completely prior to flow reversal will
pass through the reactor in two directions, i.e. as forward and backward flows. Such gas elements show a residence time distribution, spreading from zero to \(2\tau_0\). Therefore, the calculation of the average gas residence time requires an integration over the contribution of all gas elements during one-full cycle. Similar reasoning holds for a switching time less than the gas residence time in once-through operation, but in that case particular attention must be paid to the gas dead volume, which is trapped inside the reactor.

Two situations are considered: \(\alpha \leq 1\) and \(\alpha > 1\). If the bed porosity is assumed uniform along the reactor and the superficial velocity remains constant, the average residence time when flowing from \(z = 0\) to \(z = L\) and from \(z = L\) to \(z = 0\) is the same. \(L\) is the distance from the reactor entrance to the maximum axial position that can be reached by the leading gas when the flow direction is reversed.

**Case \(\alpha \leq 1\)**

In the case of \(\alpha \leq 1\), the switching time obviously indicates the maximum residence time of the fluid element for one trajectory. The residence time of the fluid element is prevalently distributed from 0 to \(t_s\) for flow in one direction. When \(\alpha < 1\) prevails, the gas in the center part of the reactor is trapped, while the reaction in this part is still ongoing until the limiting reactant has disappeared. The fresh gas fed into the reactor will not pass through the reactor completely. This fresh gas will be retained by the trapped gas and pushed backward through the reactor when feed gas enters the reactor from the opposite side. In this case, the average residence time of the gas can be written as in Equation 3-1:

\[
\tau_{avg} = \frac{\int_0^L \tau(z)\,dz}{\int_0^L dz} \tag{3-1}
\]

The gas residence time \(\tau(z)\) of an individual element obviously depends on the trajectory, passed when flowing through the reactor. In the case of RFO with \(\alpha \leq 1\), \(\tau(z)\) can be expressed as follows, taking forward and backward flows into account:

\[
\tau(z) = 2\frac{\varepsilon_b}{u_s}z \tag{3-2}
\]

Subsequently, solving Equation 3-1 by substituting \(\tau(z)\) with Equation 3-2 yields Equation 3-3:
CHAPTER 3. Reverse Flow Operation

\[
\tau_{\text{avg}} = \frac{2 \varepsilon_b L}{u_s} \frac{\int z \, dz}{L} - \frac{2 t_s L}{L} \frac{\int z \, dz}{L} = t_s
\]  

(3-3)

where \( \varepsilon \) is the bed porosity and \( u_s \) is the superficial velocity.

**Case \( \alpha > 1 \)**

During one-half cycle \( (t_s) \), part of the gas will completely pass through the reactor in one direction with a residence time of \( \tau_o \). In the same flow direction, another part of gas passes through the reactor partially with a distributed residence time, depending on the position where a gas element ends up inside the reactor when the flow direction is reversed. The latter follows the Equation 3-3 when determining the average residence time. The general formulation of the average residence time in RFO for \( \alpha > 1 \) is shown in Equation 3-4:

\[
\tau_{\text{avg}} = \left( 1 - \frac{\tau_o}{t_s} \right) \tau_o + \frac{\tau_o}{t_s} \frac{\int \tau(z) \, dz}{L_r} + \tau_o + \frac{\tau_o}{t_s} \frac{\int z \, dz}{L_r} = \tau_o
\]

(3-4)

where \( L_r \) is the reactor length.

In once-through operation, \( t_s \) will be infinite. Therefore, if the switching time is extremely large, the average residence time approaches the residence time for once-through operation. Considerations of average residence time become important when the time scale for switching is the same or less than the residence time in once-through operation.

**RESIDENCE TIME DISTRIBUTION**

The distribution of residence time for a continuous flow system has been studied by Danckwerts (1953). The gas residence time distribution during reverse flow operation is of particular interest to obtain a better insight of the gas transport through the catalyst bed, particularly when the switching time is near to the gas residence time. The residence time distribution has a distinct influence on the conversion unless the reaction rate has zero order. Figure 3-1 represents the residence time distribution during RFO for two cases, \( t_s > \tau_o \) and \( t_s \leq \tau_o \).
For $t_s > \tau_o$ (see Figure 3-1a), the gas residence time has two contributions. The pulse at $\tau_{o}$ represents the fluid that has passed the fixed bed completely. Its contribution is more pronounced whenever $t_s$ exceeds more and more $\tau_{o}$. The dotted line at $E = 1/(2t_s)$ represents elements that stay in the bed. They flow in the opposite direction if the flow is reversed. This contribution becomes minor when $t_s$ increases. Figure 3-1b shows the gas residence time distribution during RFO for $t_s = \tau_{o}$ and $t_s < \tau_{o}$. When the switching time $t_s$ is equal to the residence time $\tau_{o}$, the residence times of gas elements are distributed between 0 and $2\tau_{o}$. When the flow reversal occurs more frequently ($t_s < \tau_{o}$), the residence times are distributed between 0 and $2t_s$, excluding the gas trapped in the central part of reactor. The residence time distribution can be formulated as written in Equation 3-5:

$$E(t) = \begin{cases} 
\frac{1}{2t_s} & \text{for } 0 \leq t \leq 2\tau_{o} \text{ and } t \neq \tau_{o}, \text{ e.g. for the part of} \\
\text{the gas, which flows forward} \text{ and backward} \\
\delta(t - \tau_{o}) & \text{a Dirac } \delta \text{- function if } t = \tau_{o} \text{ with size} \\
\left(1 - \frac{\tau_{o}}{t_s}\right) & \text{e.g. for the part of the gas, which passes in} \\
\text{unidirectional flow} \\
0 & \text{for } t > 2\tau_{o} \\
\end{cases} \quad (3-5a)$$

$$E(t) = \begin{cases} 
\frac{1}{2t_s} & \text{for } 0 \leq t \leq 2t_s \\
0 & \text{for } t > 2t_s \\
\end{cases} \quad (3-5b)$$
CHAPTER 3. Reverse Flow Operation

REGIMES OF OPERATION

Because flow reversals may either disturb the steady state of a process or may prevent that a process becomes steady, three ranges of the parameter $\alpha$ can be distinguished: $\alpha >> 1$ for the quasi-steady state regime, $\alpha << 1$ for the relaxed steady state regime, and $\alpha \approx 1$ for the dynamic regime (Budhi et al., 2004a). The three regimes of RFO are illustrated by simulation results obtained with the model presented in Chapter 2. In Figure 3-2, NH$_3$ partial pressure responses are plotted versus the ratio of time over the gas residence time. The time-average value of the partial pressure ($p_{\text{avg}}$) and the value during steady state, once-through operation ($p_{\text{ss}}$), are also shown for comparison.

![Figure 3-2](image)

**Figure 3-2.**
Different types of reverse flow behaviour at different time scales. The partial pressure response of NH$_3$ at the reactor outlet is plotted as a function of time. $p_{\text{ss}}$ stands for the partial pressure of NH$_3$ in steady state, once-through operation; $p_{\text{avg}}$, $p_{\text{res}}$, and $p_{\text{dyn}}$ for quasi-steady state, relaxed steady state, and dynamic responses in reverse flow operation; $p_{\text{avg}}$ for the time-average value ($p_{\text{avg}}$ indicates RFO with flushing, see text page 57). Switching time: (a). 50 s, (b). 2 s, (c). 10 s. $T = 800$ K, $\tau_o = 10$ s, FR = 1:1. Other operating conditions as mentioned in Table 2-4. The rate parameters were taken from Rebrov et al. (2002).
• Situations with $\alpha \geq 1$ mean that flow reversals occur at low frequency, which leads to quasi-steady state behaviour because the flow direction hardly affects the time-average result. The dynamic response completely coincides with the steady state except for a short period after a flow reversal (see Figure 3-2a).

• A high flow reversal frequency ($\alpha < 1$) means that the central part of the reactor is never refreshed with fresh reactants by convection. Apparently, use of only a part of the catalyst bed causes a significant decrease of the conversion as indicated by the profound difference between $p_{\text{hug}}$ and $p_{\text{ss}}$ (see Figure 3-2b). Depending on the flow direction, this gas volume moves up- and downwards, which leads to exchange between gas phase and catalyst surface via adsorption and desorption. This amount of gas is therefore not to be considered as a real dead volume, i.e. gas trapped inside the reactor. The axial profile of the NH$_3$ concentration inside the reactor for $t_s < \tau_0$ at the end of one-half cycle is simulated in Figure 3-3. For this specific case, the dead gas volume from a view point of convection may occupy 80% of the catalyst length. However, a zone $0.2 \leq z \leq 0.6$ is a better approximation for the dead gas volume because of adsorption/desorption effects. In reality, the zone with zero NH$_3$ concentration due to ongoing reaction is even smaller ($0.28 \leq z \leq 0.48$ in Figure 3-3) because of molecular diffusion and axial dispersion. At extremely frequent flow reversals, the reactor will not respond anymore to the perturbation after stable oscillation, which should be considered as the relaxed steady state or sliding regime.

• Situations with $\alpha \approx 1$, where the perturbation and the process kinetics have comparable time scales, cause dynamic behaviour with possible involvement of resonance effects due to non-linear behaviour of the whole system (see Figure 3-2c). This regime seems most optimal if the conversion does not deviate too much from steady state conversion, while the product distribution may deviate from the steady state situation. In principle, the flow direction should be reversed when steady state is nearly reached.

Figure 3-3.
Axial profile of NH$_3$ partial pressure during RFO just before switching the flow direction from left to right. The dead gas volume region is shown by the shaded area. $T = 800 \text{ K}$, $\tau_0 = 10 \text{ s}$, $\text{FR} = 1:1$, and $t_s = 2$. 
DEAD GAS VOLUME

The gas hold-up in the center part of the reactor may become a dead gas volume when $\alpha$ is less than 1. This dead gas volume will never reach the reactor outlet. It moves up and down in the center of the catalyst bed, depending on the flow direction. The existence of this dead gas volume may become interesting for manipulation of catalyst surface coverage. The dead gas volume hardly contains reactants as the reactions will tend to completion. Therefore, such trapped gas becomes superfluous and should be flushed on a regular basis in order to generate new reaction potential. Without flushing the reaction continues until the limiting reactant is completely converted.

The time-average conversion during RFO is obtained from the active zone only, where the feed gas enters the reactor and the products flow out. The trapped gas in the center part of the reactor is not involved. If the trapped gas containing a lot of reaction products is regularly flushed via periodic once-through operation, it would provide an extra contribution to conversion and selectivities.

In order to achieve stable oscillations during reverse flow simulation with $\alpha < 1$, it basically requires larger CPU times than at low flow reversal frequency. Around 90-100 semi-cycles are the required order of magnitude to reach stable oscillations when $\alpha = 0.2$. The smaller $\alpha$, the larger number of cycles is needed to obtain stable cycling.

SIMULATION OF REVERSE FLOW REACTOR

Simulations were carried out for a reactor with an imposed steady temperature profile as typical for reverse flow operation, which is allowed because thermal and kinetic behaviours have completely different time scales. The thermal behaviour can be considered as in a relaxed steady state regime compared to the kinetic behaviour when the switching time is in the order of seconds. The concentration profiles as a function of time generally show stable oscillations after two full cycles in the dynamic regime and quasi-steady state regime, and dozens of cycles for the sliding regime. Therefore, a temperature profile along the reactor can be imposed. It should be noted that a temperature profile could be directly measured during experimental work in reverse flow reactors. Isothermal reactor operation on a laboratory scale can be achieved when there is good heat transfer between reactor and environment. This holds especially if feed concentrations are low, limiting the maximum adiabatic temperature rise. The simulation focused on the influence of the reverse flow operation on conversion and selectivity and is compared to the steady state operation.
The steady state results were inspected with respect to the occurrence of pronounced axial profiles of gas phase concentrations and/or catalyst surface coverages. Conceivably, such profiles are most likely affected by applying reverse flow operation. Reverse flow simulations were therefore performed at conditions that gave rise to pronounced axial profiles at SSO.

NON-ISOTHERMAL SIMULATION

The reactor model equations were based on mass balances as presented in Chapter 2. In practice, adiabatic operation of a reverse flow reactor is never achieved because it would lead to ever increasing temperatures inside the reactor. Therefore, a term describing heat transfer through the reactor wall to the environment should be added to the gas phase heat balance. Non-isothermal simulations were performed by setting the heat transfer coefficient into a rather high value to prevent too much temperature rise inside the reactor, which would cause numerical instabilities when solving the system. Once the temperature profile during reverse flow operation has been established (see Figure 2-2), there is no need to incorporate heat balances into the reactor model. It should be sufficient to impose a symmetrical temperature profile along the reactor axis when the time scale for reversing the flow direction is in the order of seconds. On this time scale, the developed temperature profile can hardly respond to perturbations due to flow reversals. At either end of the reactor, the temperature equals the feed temperature, and the maximum temperature in the middle of the reactor corresponds to the maximum adiabatic temperature rise, corrected for heat losses. In this case, the feed gas temperature was set at 800 K, and the maximum temperature in the middle of the reactor was 810 K.

SIMULATION RESULTS

Regular reverse flow operation

Figure 3-4 shows typical simulation results of the NH₃ conversion and selectivities to N₂, NO, and N₂O during reverse flow operation (Budhi et al., 2004a). The values are indicated as the difference between the reverse flow operation and the steady state, once-through operation versus dimensionless switching time over residence time for once-through operation (τₒ). Temperature, residence time, and feed oxygen concentration were kept constant. At low flow reversal frequency, conversion and selectivities approach the steady state values as expected. Only minor differences in the various selectivities due to RFO are observed. The time-average conversion of
NH₃ during reverse flow operation is always lower than that of once-through operation, regardless of α. The conversion decrease is most pronounced at high flow reversal frequency, which is caused by the existence of the dead gas volume. In this case, only part of the catalyst bed is directly used by the inlet gas to perform the reaction, which corresponds to an average residence time equal to the switching time (see Equation 3-3). The rest of the catalyst, standing in the reactor center, is never reached by the inlet gas. It means that the feed with high reactant concentration, which just entered the reactor, only contacts the catalyst in the outer part of the reactor and then flows out again when the flow direction is reversed. Another factor affecting the conversion decrease is the lower amount of adsorbed oxygen on the catalyst surface coverage when comparing RFO and SSO. The adsorbed oxygen profiles during SSO are invariant over the time and the differences between oxygen coverage at the reactor inlet and outlet are relatively small. As can be seen in Figure 3-5, the oxygen coverage at various axial positions in RFO changes considerably over time. Significant fluctuations of the oxygen coverage occur at the reactor outlets, both at z = 0 and z = 1, depending on the flow direction. Shortly after reversing the flow direction, oxygen coverage still occupies a high fraction of the surface. This fraction drops quite considerably to a minimum value and increases up again when time proceeds. The pronounced decrease of oxygen coverage is induced by the double trajectory of the component oxygen when the flow direction is reversed again. It means that the period of consuming adsorbed oxygen is also longer, leading to a lower oxygen coverage and lower conversion of NH₃ as well.

![Figure 3-4](image)

*Figure 3-4.* Simulated conversion and selectivity for ammonia oxidation in regular RFO as a function of the switching time. Data are presented as difference between RFO and SSO performance. T = 800 K, τₒ = 10 s, and FR = 1:1 (adopted from Budhi et al. (2004a)). The kinetic rate parameters were taken from Rebrov et al. (2002).

In Figure 3-6, the behaviour of reactants and products during RFO in the sliding regime are presented. This simulation was run for isothermal conditions, starting from the steady state at t = 0. Stable oscillations are
achieved after around 90-100 semi-cycles, depending on $\alpha$. Ammonia shows a full conversion in the dead volume region (see Figure 3-6a). The trapped reaction products, particularly N\textsubscript{2} and NO, have much higher concentration levels in the dead gas volume region than in the region where the incoming and outcoming flows occur. The differences between the flown-through and non-flown-through regions are also reflected by the surface coverages, depicted in Figure 3-6b. In the dead gas volume, the coverages of vacant sites {\(\cdot\)} and (\(\cdot\)), as well as (O), and \{NO\} are high, while (OH), \{NH\textsubscript{3}\}, and (N) are low. Almost no (OH) is detected along the reactor due to the fast desorption of (OH) to produce H\textsubscript{2}O. This condition favours the selectivity to deep oxidation.

Figures 3-6c, d, and e show the evolution of the partial pressures of N\textsubscript{2}, NO, and N\textsubscript{2}O over time since the start of the flow reversals at time $t = 0$. Each evolution is plotted for two axial positions, $z = 0$ and $z = 0.5$. As mentioned before, many flow reversals are required to obtain stable oscillations, i.e. the transient profiles during one-half cycle are completely identical to the profiles in the subsequent one-half cycle. Stable oscillation occurs earlier at $z = 0$ than at $z = 0.5$. One should realize that the oscillations at $z = 1$ are identical to the ones at $z = 0$. Their appearance as a function of time is only one switching time later. The reactions in the central part of the reactor proceed until all reactants vanish. Then the reactions stop or attain equilibrium and stable oscillations arise. When the ammonia in the central part of the reactor is completely converted or a desired product has attained a certain level, flushing the reactor could be accomplished to collect the trapped product.
Figure 3-6. Simulated RFO in the sliding regime: partial pressures of NH₃, N₂, NO, and N₂O (a) and surface coverages (b) along the reactor at the end of a cycle before switching the flow direction; typical development of the partial pressures of N₂ (c), NO (d), and N₂O (e) as a function of time-on-stream at axial positions z = 0 and z = 0.5. Conditions: T = 573 K, τ₀ = 0.6 s, FR = 1:3, tₛ = 0.3 s. For (a) and (b), t = 27 s.
An interesting behaviour in the sliding regime of RFO is the different concentration level of the reaction products in the trapped region and in the flow region. As can be seen in Figures 3-6c and d, the concentrations of N₂ and NO are obviously higher in the reactor centre than at the reactor outlet. The opposite situation holds for N₂O (see Figure 3-6e). It could be that N₂O dissociates to N₂ in the reactor centre, while a higher oxygen coverage on the catalyst surface favours NO production. If N₂O is favoured as the desired product, RFO in the sliding regime without periodic flushing should be preferred. If N₂ or NO is favoured, periodic flushing would give a better performance.

**Flushing operation**

In the sliding regime of RFO, the unconverted reactants and reaction products in the reactor centre are trapped. The limiting reactant might be completely converted into products if the reactor is continuously maintained in reverse flow mode. In order to gain the trapped products and to feed the central part with reactants again, periodically flushing the trapped gas by a short once-through operation might be an interesting option. The time-average conversion of NH₃ will increase by periodic flushing, and the product distribution will change accordingly.

The conversion of NH₃ and the selectivities towards N₂, NO, and N₂O during regular reverse flow operation plus periodic flushing are presented in Table 3-1 for a specific case. Table 3-1 also compares the RFO without flushing. After every 5 cycles of 2 s, the gas content of the bed was flushed for a period of 10 s, which is the same as the residence time for once-through operation. The time-average NH₃ partial pressure, \( p_{\text{tavg}} \), in the trapped region will attain a lower level than the time-average NH₃ partial pressure in regular RFO in the sliding regime. It means a better conversion can be achieved when combining regular RFO and flushing (Figure 3-2b). However, as appears from Table 3-1, the conversion is still lower than in the steady state. The same holds for RFO with longer switching times. The selectivity is hardly affected. For this reason the flushing operation was not optimized.

**Product distribution as an effect of flow reversal**

As obviously shown in Table 3-1, RFO affects the product distribution, albeit minor. Therefore, the relation between conversion and selectivity was considered in order to make certain that selectivity changes are substantially caused by reverse flow operation, and not as a result of the change in conversion.
Table 3-1. Simulated conversion and selectivity difference ($\Delta$, RFO - SSO) compared for regular RFO and RFO plus flushing. In the flushing operation, the reactor is flushed during 10 s after 5 times one-half cycle. Operating conditions: $T = 800 \text{ K}$, $\tau_o = 10 \text{ s}$, $t_s = 2 \text{ s}$, FR = 1:1. Other conditions as mentioned in Table 2-4.

<table>
<thead>
<tr>
<th></th>
<th>Without flushing</th>
<th>With flushing #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Switching time, s</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\Delta$ Conversion of NH$_3$, %</td>
<td>-49.6</td>
<td>-28.0</td>
</tr>
<tr>
<td>$\Delta$ Selectivity to N$_2$, %</td>
<td>+2.0</td>
<td>+1.4</td>
</tr>
<tr>
<td>$\Delta$ Selectivity to NO, %</td>
<td>-2.4</td>
<td>-0.2</td>
</tr>
<tr>
<td>$\Delta$ Selectivity to N$_2$O, %</td>
<td>+0.4</td>
<td>-1.2</td>
</tr>
</tbody>
</table>

# 5 times in one-half cycle, then flushed during 10 s.

Table 3-2 simply compares the simulation results for SSO and RFO at the same temperature and feed ratio, but different residence time in order to maintain the same conversion. Steady state operation with a residence time of 1.1 s and RFO with a residence time of 10 s and switching time of 0.5 s provide the same conversion of 17.3%. Note that the product distributions are different. This example clearly implies that the differences in product distributions are substantially caused by reverse flow operation. The effect of reverse flow operation on the selectivity may be positive or not, depending on the chosen process conditions and the actually desired product (Budhi et al., 2004a).

Table 3-2. Comparison of simulated conversion and selectivity for SSO and RFO at the same conversion with operating conditions as mentioned in Table 2-4. $T = 800 \text{ K}$, FR = 1:1.

<table>
<thead>
<tr>
<th></th>
<th>SSO</th>
<th>RFO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residence time, s</td>
<td>1.1</td>
<td>10</td>
</tr>
<tr>
<td>Switching time, s</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Conversion of NH$_3$, %</td>
<td>17.3</td>
<td>17.3</td>
</tr>
<tr>
<td>Selectivity to N$_2$, %</td>
<td>34.1</td>
<td>32.6</td>
</tr>
<tr>
<td>Selectivity to NO, %</td>
<td>56.0</td>
<td>59.6</td>
</tr>
<tr>
<td>Selectivity to N$_2$O, %</td>
<td>9.9</td>
<td>7.8</td>
</tr>
</tbody>
</table>

EXPERIMENTS

The experimental study of a reverse flow reactor for selective oxidation of ammonia was conducted in a laboratory scale reactor. The experiments under RFO aimed to explore its potential compared to the SSO. The experimental set-up and procedures, including catalyst pretreatment and line-out procedure, have been described in Chapter 2. The steady state experiments were described in Chapter 2 as well.
RESULTS AND DISCUSSION

TRANSIENT PROFILE

Figure 3-7 shows a typical transient profile of NH$_3$ as a function of time observed during regular RFO. During the periods of 0-15 s and 30-45 s, the profile of NH$_3$ corresponds with the inlet concentration, while during the period of 15-30 s, the outlet NH$_3$ concentration is monitored. The model can describe well the experimental result. Shortly after reversing the flow direction at 15 s, the concentration of NH$_3$ measured at the reactor outlet drops significantly and reaches the steady state level. The concentration of NH$_3$ increases again to the inlet level when the flow direction is reversed as can be seen at 30 s.

Figure 3-7. Concentration profile of NH$_3$ (markers) and model predictions (lines) as a function of time in regular RFO. Conditions: T = 673 K, $\tau_o = 0.6$ s, FR = 1:1.

EFFECT OF SWITCHING TIME

The switching time is a crucial parameter in reverse flow operation, as it determines the operation regime. In these series of experiments, the switching time was varied from 2.5 s till 30 s, while the residence time was 0.6 s. It means that most experiments were done in the quasi-steady state regime, while the shorter switching times approach the dynamic regime. Switching times, shorter than 2 s, could not be applied due to limitations of the switching valves. They would induce serious axial dispersion at the reactor inlet affecting the step-wise concentration changes.

Figure 3-8 shows model predictions and experimental results in terms of conversion and selectivity versus switching time during regular reverse flow operation at 673 K and a 1:1 feed ratio of ammonia to oxygen. Similar results can also be seen in Figure 3-9, but for a temperature of 573 K and a feed ratio
of ammonia to oxygen of 1:3. The experimental data on the ammonia conversion demonstrate that the time-average conversion during RFO approaches to the value in SSO if the switching time becomes larger.

![Figure 3-8](image1)

**Figure 3-8.** Experimental results (markers) and model predictions (lines) for NH$_3$ conversion and selectivities to N$_2$, NO, and N$_2$O as a function of switching time in regular RFO. Data are presented as difference between RFO and SSO. Conditions: T = 673 K, $\tau_o = 0.6$ s, FR = 1:1.

![Figure 3-9](image2)

**Figure 3-9.** Experimental results (markers) and model predictions (lines) for NH$_3$ conversion and selectivities to N$_2$, NO, and N$_2$O as a function of switching time in regular RFO. Data are presented as difference between RFO and SSO. Conditions: T = 573 K, $\tau_o = 0.6$ s, FR = 1:3.
In regular RFO, the conversion of ammonia is always lower compared to the conversion in SSO. The decrease of ammonia conversion seems more pronounced when the regime operation gradually shifts to the relaxed steady state as also shown by the model.

The decrease of the ammonia conversion during RFO is induced by different factors. First, the high concentration of ammonia near the reactor entrance is driven out when the flow direction is reversed. The low conversion of ammonia in that part obviously has a significant contribution to the time-average conversion of one complete cycle. The residence time of the gas that only reaches the beginning of the reactor is shorter than the residence time of the gas that penetrates further toward the reactor centre. Second, the adsorbed oxygen on the catalyst surface shortly after reversing the flow direction may also contribute to the decrease of ammonia conversion. Shortly after reversing the flow direction, oxygen coverage suddenly occupies a high fraction of the surface. This fraction drops subsequently to a slightly low level before finally it reaches the steady state level (see at \( z = 1 \) Figure 3-10). This profile behaviour shifts in parallel with the flow direction as can be seen at \( z = 0.5 \) and \( z = 0 \). The decrease of oxygen coverage is induced by the double trajectory of component oxygen when the flow direction is reversed again. It means that the period of consuming adsorbed oxygen is longer. As consequence, the conversion of NH\(_3\) in RFO is lower than in SSO. Similar behaviour was also seen in Figure 3-5.

The observed selectivities at large switching times have similar values as observed during SSO, which should be expected. At short switching times, the selectivity to N\(_2\) exceeds the steady state levels, while the opposite holds for N\(_2\)O and NO (Figures 3-8 and 3-9). The effects are more pronounced in Figure 3-9, which concerns lower temperature and higher oxygen content of the feed.
Here, at intermediate switching times, there is a distinct increase of the N₂O selectivity at the expense of the N₂ selectivity, while the NO selectivity remains at a clearly lower level in comparison to the steady state. Similar trends can be seen in Figure 3-8, but all effects are smaller.

Drawn curves in Figures 3-8 and 3-9 refer to model predictions as obtained with the model presented in Chapter 2. The NH₃ conversion changes, when comparing RFO and SSO in Figure 3-8, are overestimated at low switching times. At lower temperature and higher oxygen content of the feed (Figure 3-9), model predictions and observation are in line. Selectivity predictions in Figure 3-8 are better than in Figure 3-9. In spite of the deviations in Figure 3-9, the model predicted trends follow the observations. With increasing switching time, the N₂ selectivity decreases down to a minimum value and then slightly increases to the quasi-steady state value. Similarly, the N₂O selectivity increases up to a maximum before reaching the steady state level, as is in line with the trend of the data. In Figure 3-8 model predictions follow the trend of the data as well. Here, it seems that quasi-steady state values of the selectivity changes are reached at shorter switching time than occurs in Figure 3-9. It seems likely that deviations between model prediction and experiments are due to some imperfection of the kinetic model, notably regarding secondary reactions (see page 40). Trends, however, seem to be predicted well.

EFFECT OF RESIDENCE TIME

In the conventional application of RFR, a change of the flow rate induces a pronounced change of the reactor temperature. This is especially evident in a laboratory reactor where heat loss from the reactor cannot be ignored (Matros and Bunimovich, 1996). Increasing the flow rate may diminish the contact time, leading to extinction of the reaction. Obviously, a larger gas residence time may lead to lower temperatures and extinction as well. It is important therefore to predict the gas residence time domain, where RFR can be operated (Ben-Tullilah et al., 2003).

For the manipulation of catalyst surface coverage by RFR, the relation between the residence time and the switching time is very fundamental in determining the operation regime. If the switching time is much larger than the residence time is, the effect of flow reversal on the conversion and selectivity becomes less and both quantities approach to the steady state level. Figure 3-11 presents experimental results for NH₃ conversion and selectivities to N₂, NO, and N₂O as a function of residence time in regular RFO. An increase of the residence time at constant switching time induces a larger decrease of the ammonia conversion difference between RFO and SSO, which trend is confirmed by the model prediction. Increasing the residence time at constant switching time shifts the operation to the direction of the sliding regime. Even if the operation regime might be still in the quasi-steady state,
such movement will contribute to the decrease of conversion, which is more pronounced when switching time over residence time is smaller. It was previously mentioned that the conversion of ammonia in the sliding regime in regular RFO is always lower than in SSO.

The selectivity to NO decreases if the residence time increases, while the selectivities to N$_2$ and N$_2$O increase. It is possible that NO in the reactor decomposes and/or interacts with NH$_3$ to produce N$_2$ (Perez-Ramirez et al., 2004, 2005). Again this underlines the importance of the secondary reactions for the kinetic model. The model predicts that the product distribution would not change because the operation regime is still in the quasi-steady state.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3-11.png}
\caption{Experimental results (markers) and model predictions (lines) for NH$_3$ conversion and selectivities to N$_2$, NO, and N$_2$O as a function of residence time in regular RFO. Data are presented as difference between RFO and SSO. Conditions: T = 573 K, FR = 1:3, t$_s$ = 5 s.}
\end{figure}

**EFFECT OF TEMPERATURE**

Besides the switching time, the temperature also plays a significant effect. Figure 3-12 depicts the effect of temperature on the conversion and selectivity differences when RFO and SSO are compared. At 673 K, the change of the NH$_3$ conversion is more pronounced than at 573 K. In contrary, the product distribution differences between RFO and SSO are less pronounced at 673 K. Increasing the temperature obviously causes the reaction rates to increase, while the dynamic influence due to flow reversal becomes less, which might lead to a stronger influence on the conversion of unconverted reactants after a flow reversal. A similar behaviour is also seen when comparing Figures 3-8 and 3-9, albeit that there exists a difference in the NH$_3$/O$_2$ ratio as well between these figures. Nevertheless, the higher temperature of Figure 3-8 seems to induce that the quasi-steady state regime is already observed at smaller ratios of the switching time over residence time. Ideally, to reduce the decrease of NH$_3$ conversion due to the faster reaction rate at higher temperature, the switching time should be set at larger time periods.
The selectivity differences between RFO and SSO become less at 673 K compared to 573 K. This is in line with simulations showing that at even higher temperature the product distribution changes due to flow reversal are minor. The results of Figures 3-8 and 3-9 confirm this point as well. As the reactions proceed at larger rate, the dynamics of the reactor relatively tend to decrease as effectuated by smaller deviations from the steady state conditions. Effects of temperature on the product distribution as expected during steady state operation are still present in this case, where the selectivity to N₂ decreases and selectivities towards NO and N₂O go up at higher temperature.

**EFFECT OF OXYGEN CONCENTRATION**

*Figure 3-13* illustrates the effect of the oxygen feed concentration on the NH₃ conversion and selectivities to N₂, NO, and N₂O. The conversion of ammonia is hardly changed by increasing the oxygen concentration from 2 vol.% to 3 vol.% because it has already reached a high level during the steady state operation. With increasing oxygen concentration, the difference in conversion between RFO and SSO is slightly larger because the conversion increase in SSO is higher than in RFO. The model prediction of the NH₃ conversion also decreases when the oxygen concentration is higher. However, the model prediction slightly overestimates the experimental result.

The changes of the selectivity (RFO-SSO) towards N₂ decrease when increasing the oxygen feed concentration. At higher oxygen concentration, a higher oxygen surface coverage would stimulate the production of oxygen containing products as to be expected in SSO. This trend is confirmed by the selectivity changes with respect to N₂O, which turn from negative to positive when the oxygen feed content increases. For NO the selectivity changes become more negative. The product distribution for steady state operation favours N₂ and N₂O at 573 K. The model prediction, as indicated by dots in
Figure 3-13, show smaller effects than observed experimentally, but the trend of the predictions follows the data.

**Figure 3-13.** Experimental results for NH₃ conversion and selectivities to N₂, NO, and N₂O as a function of oxygen concentration in regular RFO. Conditions: T = 573 K, τₜ = 0.6 s, FR = 1:2 and 1:3, tₛ = 5 s. The dots show the model prediction.

### EFFECT OF ASYMMETRIC TIME PERIOD

An asymmetric switching time is another option when exploring the behaviour of reverse flow operation from a viewpoint of selectivity manipulation. It can be performed by applying a different time period between forward and backward flows (tₛ→ ≠ tₛ←, but tₛ→ + tₛ← = t₉). In principle, such kind of operation procedure may create other unique coverages of the active sites because the profile development of the adsorbed species along the reactor is different for the two flow directions. The real phenomena that occur during the operation are more complicated due to the fact that a lot of process variables are involved. In this study, observation was focused on two different switching times, i.e. at tₛ = 2.5 s and tₛ = 5 s. The comparison between symmetric and asymmetric RFO is given in Table 3-3.

**Table 3-3.** Experimental results of NH₃ conversion and selectivities to N₂, NO, and N₂O for symmetric (Sym.) and asymmetric (Asym.) regular RFO. The switching time during symmetric RFO is the same, 50% of cycle time for each flow direction, while during asymmetric RFO, it is 25% and 75% of cycle time for left to right and for right to left, respectively. Conditions: T = 673 K, τₜ = 0.6 s, FR = 1:5.

<table>
<thead>
<tr>
<th></th>
<th>tₛ = 2.5 s</th>
<th></th>
<th>tₛ = 5 s</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ Conversion of NH₃, %</td>
<td>-15.0</td>
<td>-28.4</td>
<td>-8.5</td>
<td>-22.7</td>
</tr>
<tr>
<td>Δ Selectivity to N₂, %</td>
<td>11.6</td>
<td>10.7</td>
<td>9.3</td>
<td>9.2</td>
</tr>
<tr>
<td>Δ Selectivity to NO, %</td>
<td>-12.9</td>
<td>-10.8</td>
<td>-11.0</td>
<td>-9.4</td>
</tr>
<tr>
<td>Δ Selectivity to N₂O, %</td>
<td>1.3</td>
<td>0.01</td>
<td>1.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>
As can be seen, the conversions of NH$_3$ indicate a lower value during asymmetric RFO than during symmetric RFO for both cases. It means that the shorter time period, i.e. 25% of cycle time, in asymmetric RFO might contribute more significant to the decrease of the NH$_3$ conversion, which results in a lower overall conversion. In both cases, the selectivity changes towards each component are slightly less for asymmetric RFO than for symmetric RFO case.

**CONCLUDING REMARKS**

A mathematical model and an analysis of reverse flow reactor behaviour at switching times in the order of seconds are required to study selectivity manipulation via reverse flow operation. A switching time close to the gas residence time is typically necessary. Three operation regimes concerning the ratio of the switching time over the gas residence time were studied, i.e. the quasi-steady state regime, the relaxed steady state regime, and the dynamic regime. A dead gas volume may occur if the switching time is less than the gas residence time. A flushing method may become an interesting option to refresh such dead volume with fresh feed. An increase of conversion was found when comparing RFO plus flushing to regular reverse flow operation. The selectivities were changed as well.

Regular RFO always invokes a conversion decrease as observed during the experiments and model validation. This major drawback of regular RFO is most pronounced at shorter switching time. It was also found that the selectivity was rather insensitive to changes in the switching frequency. An increase of the gas flow rate at constant switching time basically shifts the operation regime towards the relaxed steady state. The reaction temperature and the oxygen concentration may affect the conversion and selectivity in RFO, which effect might be positive or negative, depending on their relative influence. The oxygen coverage changes only shortly after reversing the flow direction. Asymmetric RFO may induce even a larger conversion decrease, while it may influence the product distributions. Model predictions follow the trends of experimental data. Deviations, however, are present and seem due to imperfection of the kinetic model, notably the secondary reactions.

In order to prevent the conversion decrease in regular RFO, a novel concept of reverse flow operation is indispensable. This topic will be presented in the subsequent chapters, so called RFO with temporarily lower feed concentration (Chapter 4), and RFO with reactor side feeding (Chapter 5).
Chapter 4

Reverse Flow Operation with Temporarily Lower Feed Concentration

You are considered to be an expert if you can make your grand mother understand.
Albert Einstein

Summary
A novel concept of reverse flow operation (RFO) in combination with a periodically lower feed concentration (concentration programming) is proposed to overcome the conversion drop during regular RFO. The time period of lower feed concentration is a crucial variable, which strongly influences the conversion and selectivity. The effects of temperature, gas residence time, and feed oxygen concentration are considered as well. The model and experimental results indicate that the novel reactor concept can be applied for manipulation of selectivity. The NH₃ conversion in RFO with concentration programming increases compared to regular RFO and may even exceed the conversion during steady state operation. The adsorbed O enrichment on the catalyst surface due to lowering the NH₃ concentration in the feed increases the NO selectivity. The production rate drops considerably, but the productivity is increased.
During regular reverse flow operation (RFO), the feed concentration is maintained constant over time. The time-average conversion during regular reverse flow reactor (RFR) in the kinetic regime is always lower than during steady state operation (SSO). A major reason for a lower conversion during regular RFO compared to SSO deals with the fact that the high concentration of reactant near the reactor entrance is flown out at very low conversion when reversing the flow direction. This topic has been presented in Chapter 3. In this Chapter 4, the novel concept of reverse flow operation with temporarily lower feed concentration is introduced.

INTRODUCTION

The treatment of organic gaseous emissions by combustion in catalytic reverse flow reactors was the subject of many researches in the past years. The operation under flow reversal makes it possible to treat lean gas mixtures with a lower consumption of auxiliary fuel. Nevertheless, some practical aspects concerning the application of this technology to real industrial plants have been scarcely investigated so far. One of these is the effect of unsteady characteristics of the pollutant flow, especially for plants where the operation schedule produces periodical variations in the inlet concentration and flow rate (Cittadini et al., 2001). The main consequence of periodic concentration variations is the fluctuation of the outlet concentration and of the maximum temperature in the reactor, which is much larger than the maximum temperature met during constant feeding. The continuous increase and decrease of the maximum temperature give rise to corresponding fluctuations of the outlet concentration, while in the case of constant feeding, its value is steady (Cittadini et al., 2001). The average conversion in the case of periodic feeding was reported even higher than in the case of steady feeding, depending on the feeding cycle and the time period of lower feed concentration. Cittadini et al. (2001) also observed the emission of a small amount of untreated gas at every flow reversal due to the presence of a dead gas volume in the reactor and in the piping. To avoid the dead gas volume, flow reversal at low frequency was applied. Budhi et al. (2003b) also observed the existence of the dead gas volume when the flow reversal occurs at high frequency, particularly in the sliding regime ($t_s < t_o$). The proper solution to avoid the dead gas volume is by reversing the flow direction at a switching time that is at least equal to the gas residence time for once-through operation. Van de Beld and Westertep (1994) investigated the effects of a temporary decrease in the inlet concentration. A sudden reduction in the maximum temperature occurs, but the system may recover the pseudo-steady state in a few minutes when the regular inlet concentration is restored. Snyder and Subramaniam (1993) investigated the same subject for the oxidation of SO$_2$ to SO$_3$. The control system of a reverse flow reactor for the same oxidation reaction was studied and tested by Xiao et al. (1999) via simulation of a
continuous variation in the inlet concentration. Only few data about fluctuating inlet concentrations can be found in the literature.

As previously mentioned in Chapter 3, applying the concept of flow reversal in the kinetic regime for manipulation of catalyst surface coverage requires rather frequent changes of the flow direction in order to assess the dynamic behaviour. Unfortunately, it always gives rise to a pronounced decrease of the NH$_3$ conversion. The conversion decrease is mainly caused by an outflow of unconverted reactant shortly after reversing the flow direction. This amount of gas actually had a shorter residence time and therefore higher reactant concentration compared to the rest of the reactor’s gas hold-up. This inefficient way of working could be avoided by periodically lowering the feed concentration for a short period before the flow direction is alternated (Budhi et al., 2004a). In this way, a waste of raw material in the feed is deliberately avoided, which could be considered as feed stock saving.

**MODELING OF RFO WITH TEMPORARILY LOWER FEED CONCENTRATION**

In Figure 4-1, a typology of the investigated periodic feed concentration is presented, i.e. square-wave periodic fluctuations between maximum and minimum concentrations for both forward and backward flows. The parameter $t_H$ represents the time period of high feed concentration during one half-cycle. During the rest of the half-cycle, e.g. $t_L$, the feed concentration is low. $t_H + t_L$ equals the switching time $t_s$. A periodically lower feed concentration of NH$_3$ before reversing the flow direction is deliberately actuated, while the concentration of O$_2$ remains constant over time. Increasing the feed ratio of O$_2$ over NH$_3$ as a result of a periodically lower ammonia concentration in the feed may lead to an increased oxygen coverage on the catalyst surface. In principle, this procedure is useful to increase the selectivity toward NO.

![Figure 4-1](image)

*Figure 4-1.* Square-wave periodic feed concentration in reverse flow operation. $t_H$ and $t_L$ denote the time period during which the inlet concentration is high and low, respectively. $t_s$ represents the switching time.
The mass balances of the reverse flow reactor model for both the gas phase and solid phase have been presented in Chapter 2, Table 2-1. The definition of the time-average outlet concentration remains the same. Concerning the initial values and boundary conditions, only the inlet concentration of NH₃ requires an adaptation when lowering the feed concentration (see Table 4-1). Equation 4-1 exhibits the ideal square wave of the NH₃ concentration as applied in the reverse flow operation. A value $C_{NH₃}$ is assumed during $t_H$ and a value 0 during $t_L$. The time-average inlet concentration of NH₃ is calculated as shown in Equation 4-2. The calculation of the conversion and selectivity during reverse flow operation with temporarily lower feed concentration still follows the aforementioned definitions (see Chapter 2).

**Table 4-1. Model equations of inlet concentration programming in RFO.**

| $C_{NH₃}^0(t)$ | $C_{NH₃}$ at $t \in [2(n-1)t_s, (2n+f-2)t_s]$ | 0 at $t \in [(2n+f-2)t_s, 2(n-0.5)t_s]$ | $C_{NH₃}$ at $t \in [2(n-0.5)t_s, (2n+f-1)t_s]$ | 0 at $t \in [(2n+f-1)t_s, 2nt_s]$ |

where $f$ is the time fraction for high concentration and $n$ is the number of cycles.

Time-average concentration of NH₃ in the feed for one full cycle:

$$C_{NH₃}^0 = \frac{1}{t_c} \left[ \int_{z=0}^{t_c} C_{NH₃}^0(t) dt + \int_{t_s}^{t_c} C_{NH₃}(t) \Big|_{z=L_r} dt \right]$$

(4-2)

**ANALYSIS OF RFO WITH TEMPORARILY LOWER FEED CONCENTRATION**

**TRANSIENT PROFILE**

The transient profiles of the simulated partial pressure of NH₃ as a function of time in RFO with temporarily lower feed concentration are shown in Figure 4-2 for various axial positions. The switching time is 10 s and the time period of lower feed concentration ($t_L$) is 3 s. During the period of 140-150 s, the gas
flows from right to left. The partial pressure of NH\(_3\) at \(z = 1\) is 0.01 atm. This value is maintained during the first 7 s after each flow reversal. During 3 s before the flow is directed from left to right (at 150 s), the partial pressure of NH\(_3\) is lowered to zero in order to prevent concentration losses when reversing the flow direction. This also leads to lower partial pressure at \(z = 0.8\), see at time 148-150 s. After the change of the flow direction at 150 s, the position \(z = 1\) becomes reactor outlet. The partial pressure at \(z = 1\) now gradually increases from a zero level (see 150-154 s) instead of a gradual decrease from an inlet level, which shows the concentration losses. During the rest of this half-cycle (154-160 s), the partial pressure at \(z = 1\) remains low due to the catalytic reaction. At 160 s, the whole cycle repeats with flow from right to left.

**Figure 4-2.**
Simulated partial pressure of NH\(_3\) at discrete dimensionless axial positions as a function of time in RFO with temporarily lower feed concentration. Conditions: \(T = 800\) K, \(\tau_0 = 10\) s, O\(_2\) concentration 1 vol.\%, NH\(_3\) concentration either 1 or 0 vol.\%, \(t_s = 10\) s, and \(t_L = 3\) s.

**EFFECT OF TIME PERIOD OF LOWER FEED CONCENTRATION ON CONVERSION AND SELECTIVITY**

**Figure 4-3** shows the influence of \(t_L\), the period of lower feed concentration, on the NH\(_3\) conversion and the selectivities towards N\(_2\), NO, and N\(_2\)O, all represented as the absolute difference between the values for RFO and for SSO. The conversion and selectivities during RFO were evaluated as time-average values over a full cycle. \(t_L = 0\) means that the reactor is operated under regular RFO. At low \(t_L\), RFO provides lower conversion than SSO does. But with increasing \(t_L\), the conversion of NH\(_3\) increases up to a maximum value and subsequently decreases when \(t_L\) further goes up. The maximum conversion of NH\(_3\) is reached when the time period of lower feed concentration is about 7 s. The conversion of NH\(_3\) even exceeds the steady state value when the time period of lower feed concentration is higher than 20% of the switching time. The conversion drop after passing the maximum
value is induced by a lower time-average value of the inlet NH\textsubscript{3} concentration, which is fed to the reactor. At larger time periods of lower feed concentration, NH\textsubscript{3} will be fully absent in parts of the reactor, which limits the time-average conversion of NH\textsubscript{3}. It was checked that the increase of conversion was indeed caused by the combination of temporarily lower feed concentration and flow reversal. As an example, the conversion of NH\textsubscript{3} in RFO with periodically lower feed concentration (\(\tau_o = 10\ s\), \(t_s = 10\), \(t_L = 5\ s\), \(T = 800\ K\), \(FR = 1:1\)) is about 15\% higher than in regular RFO at the same time-average inlet concentration.

As can be seen in Figure 4-3, increasing the time period of temporarily lower feed concentration gives rise to more NO, less N\textsubscript{2}, and slightly less N\textsubscript{2}O. The effect of the time period of temporarily lower feed concentration on the selectivity is monotonous, either increasing or decreasing. This tendency of the selectivity is independent of the NH\textsubscript{3} conversion. It means that inlet concentration programming directly influences the product distribution. The selectivity to NO is larger compared to N\textsubscript{2}O because the reaction temperature is high, which favours the production of NO. The selectivity to NO becomes notably larger because the reaction that produces NO is now strongly influenced by a better availability of adsorbed oxygen as will be shown later. The selectivities to N\textsubscript{2} and N\textsubscript{2}O are lower accordingly. For any value of \(t_L\), the NO selectivity is larger in RFO with concentration programming than in steady state, while the opposite holds for N\textsubscript{2} and N\textsubscript{2}O selectivities.

As far as the conversion of ammonia and the selectivity towards NO are concerned, the overall result shows that the reactor performance in the RFO with temporarily lower feed concentration is improved when compared to SSO and regular RFO.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4-3.png}
\caption{Influence of the time period of lower feed concentration on conversion and selectivity. Results are shown as difference between RFO and SSO. Operating conditions: \(T = 800\ K\), \(\tau_o = 10\ s\), O\textsubscript{2} concentration 1 vol.\%, NH\textsubscript{3} concentration either 1 or 0 vol.\%, \(t_s = 10\ s\). Conversion and selectivities for regular RFO follow from the values at \(t_L = 0\).}
\end{figure}
EFFECT OF TIME PERIOD OF LOWER FEED CONCENTRATION ON PRODUCTIVITY

Figure 4-4a depicts the productivity as a function of the time period of lower feed concentration. The definition of the productivity was already given in Chapter 2. Compared to regular RFO ($t_L = 0$), the productivities of N$_2$ and N$_2$O increase slightly up to maximum values, followed by a decrease when increasing the time period of lower feed concentration. For all $t_L$ values, the productivities of N$_2$ and N$_2$O during reverse flow operation with temporarily lower feed concentration are lower than the values in steady state, once-through operation. The increase of the NH$_3$ conversion at low $t_L$ is the major reason for the increase of productivities, both for N$_2$ and N$_2$O. The subsequent decrease of the N$_2$ and N$_2$O productivities are mainly influenced by the decrease of their selectivities. Compared to the steady state, once-through operation and regular reverse flow operation, the productivity of NO is largely improved by increasing the time period of lower feed concentration. This increase is induced by the combined effect of two factors, i.e. the increase of the ammonia conversion and the increase of the selectivity to NO. The decrease of the NH$_3$ conversion at high $t_L$ hardly influences the productivity of NO because the selectivity increase to NO at high $t_L$ is much larger.

EFFECT OF TIME PERIOD OF LOWER FEED CONCENTRATION ON PRODUCTION RATE

Though RFO with temporarily lower feed concentration causes an increase of NH$_3$ conversion and selectivity to NO, the production rate of all products decreases significantly compared to regular RFO and SSO, regardless the time period of lower feed concentration (see Figure 4-4b). The definition of the production rate was already given in Chapter 2. The decrease of the production rate is obviously induced by a lower time-average feed flow rate when inlet concentration programming is periodically actuated. As a consequence, the application of RFO with temporarily lower feed concentration requires a larger reactor or parallel reactors to maintain the production rate at a desired level, which increases the total plant investment costs. Therefore, any application should be optimized by balancing the benefits of higher productivity versus larger investments. To compromise, a full economic evaluation of the whole process including downstream processing would be necessary, which is, however, beyond the scope of this study.
CHAPTER 4. Reverse Flow Operation with Temporarily Lower Feed Concentration

Figure 4-4.
The productivity (a) and the production rate (b) as a function of the time period of temporarily lower feed concentration. Both quantities are presented as differences between the corresponding RFO and SSO values. $t_L = 0$ reflects regular RFO. Operating conditions as mentioned in Figure 4-3.

FEED STOCK SAVING

In a fixed bed reactor, the concentrations of the reactants at the reactor entrance are higher compared to their concentrations at the reactor outlet. Reversing the flow direction will therefore induce high concentration loss near the reactor inlet, built-up during the forward flow, since the inlet becomes reactor outlet during the backward flow. It leads to the conversion drop as mentioned earlier in Chapter 3. This drawback is more pronounced when the RFO requires high flow reversal frequency. Therefore, deliberately lowering the feed concentration before reversing the flow direction avoids the loss of unconverted reactants directly after the flow reversal (see Figure 4-5).

Figure 4-5.
The concentration of ammonia along the reactor axis for RFO without and with concentration programming.
This feed stock saving strategy can be compared to energy saving in conventional RFO. As a result, the preheater duty may become lower or even might be excluded. Although RFO with concentration programming provides a more efficient use of feed stock, it causes a drop of the production rate.

EFFECT OF TIME PERIOD OF LOWER FEED CONCENTRATION ON OXYGEN COVERAGE

The oxygen coverage in regular RFO is constant at the reactor inlet during the corresponding half-cycle (see Figure 3-5), while it gradually decreases and passes a minimum at all other axial positions. The minimum oxygen coverage reaches its lowest value at the reactor outlet. After passing the minimum value, the oxygen coverage at any axial position increases and eventually may reach the steady state value (see also Figure 2-8, 2-10 in Chapter 2). Although the changes of the oxygen coverage are more pronounced in regular RFO than in SSO, it was shown in Chapter 3 that the selectivity changes are minor. The same changes of the oxygen coverage, however, may also cause the conversion drop, when comparing to SSO.

Figure 4-6 shows the oxygen coverage as a function of time during one full cycle in RFO with periodically lower feed concentration. The parameter $z$ in the figure refers to the dimensionless length along the reactor axis. The oxygen coverage during RFO with temporarily lower feed concentration varies in a wide range from 0.34 to 0.90, while the oxygen coverage changes from 0.24 to 0.65 in regular RFO (see Figure 3-5). The changes are more pronounced at the reactor outlet, $z = 0$ or $z = 1$, depending on the flow direction. The time-average oxygen coverage is higher when concentration programming is applied.

Figure 4-6. Surface coverage of adsorbed oxygen during a full cycle at various axial positions for RFO with temporarily lower feed concentration. $T = 800$ K, $\tau_0 = 10$ s, $O_2$ concentration 1 vol.%, $NH_3$ concentration either 1 or 0 vol.%, $t_s = 10$ s, $t_L = 3$ s. Arrows indicate the flow direction. Other operating conditions as mentioned in Table 2-4.
Adsorbed oxygen is the major component on hollow sites at the reactor entrance when no NH$_3$ is fed to the reactor during concentration programming. Figure 4-6 shows the development of oxygen coverage at discrete axial positions in RFO with concentration programming for the case of $\tau_0 = 10$ s, $t_s = 10$ s, and $t_L = 3$ s. During the period of 140-150 s, the flow direction is from the right to the left. A steep increase of oxygen coverage occurs at the reactor inlet ($z = 1$) at $t = 147$ s, which is the time that the feed concentration of NH$_3$ is lowered to zero. When the flow direction is now reversed to the right during the period of 150-160 s, the oxygen coverage at the reactor outlet ($z = 1$) remains high for a substantial time. It gradually decreases to a minimum value before increasing again. During this cycle, the steep increase of the oxygen coverage at the reactor inlet ($z = 0$) takes place at $t = 157$ s, simultaneously when the feed concentration of NH$_3$ is lowered. This behaviour occurs periodically at every 3 s before the flow direction is reversed. The minimum value of the oxygen coverage in RFO with temporarily lower feed concentration is 0.1 higher than the minimum value in regular RFO.

It is apparent that reverse flow operation, combined with concentration programming of NH$_3$ while keeping the O$_2$ concentration constant, induces locally and temporarily high levels of adsorbed oxygen species. This condition favours NH$_3$ conversion and selectivity towards NO because the oxygen coverage may reach a high level at the reactor outlet shortly after reversing the flow direction. The moving front of adsorbed oxygen may vary, depending on the time period of temporarily lower feed concentration. In this respect, concentration programming of O$_2$ while keeping the NH$_3$ concentration constant, or concentration programming of both NH$_3$ and O$_2$, may show interesting options as well.

**EXPERIMENTS**

The experimental set-up used for the selective oxidation of NH$_3$ via RFO with temporarily lower feed concentration is similar to the one used for regular RFO as described in Chapter 3. Only a minor adaptation to the set-up was made concerning the NH$_3$ feed position. Two NH$_3$ feed lines were directly connected to the entrances of the reactor via on/off magnetic valves, positioned as near to the reactor as possible. In this way, axial dispersion in the He feed line did not affect the NH$_3$ signal anymore. Reproducible experimental data were obtained by applying the experimental procedure as described in Chapter 2. The properties of catalyst and reactor are given in Table 2-4.
CHAPTER 4. Reverse Flow Operation with Temporarily Lower Feed Concentration

EXPERIMENTAL PROCEDURE

The experimental procedure of RFO with feed concentration programming basically follows the procedure of regular RFO as already presented in Chapter 3. The time period of lower feed concentration \( t_L \) was programmed and automatically repeated at every cycle. When the concentration of ammonia is periodically lowered, the average residence time must remain the same during the whole cycle. Therefore, the helium stream was used as a balance in order to keep the total flow rate constant. The experiments were performed with variations of the time period of lower feed concentration, feed oxygen concentration, reaction temperature, and feed ammonia concentration. Concentrations were measured on-line during experiments, and the time-average behaviour was compared to the steady state operation. The data presentation is given as an absolute difference between RFO and SSO.

SIGNAL QUALITY

Separate experiments were performed to judge the quality of the reactor inlet signal during concentration programming. In this respect, it is important to determine if effects of back-mixing can be neglected during the experiments. Therefore, step response measurements with various cycle periods \( t_c \) and time period of lower feed concentration \( t_L \) were carried out using argon injection into the helium feed. In order to improve the signal quality, i.e. the square wave behaviour, a modification on the experimental set-up has been arranged by injecting the concentration programmed component directly into the feed near the reactor inlet. Figure 4-7 depicts a typical signal for conditions \( t_c = 15 \text{ s} \) and \( t_L = 5 \text{ s} \) as observed by the online mass spectrometer. Measured input signals were used as inputs for the model based simulation of RFO with temporarily lower feed concentration in order to compare experimental data and model predictions.

![Figure 4-7. Argon inlet concentration versus time for a concentration programmed experiment in once-through operation. Helium was used as balance. \( t_c = 15 \text{ s} \), \( t_L = 5 \text{ s} \). The argon mass flow controller was set at 1 vol.% for the high level and at 0.1 vol.% for the low level.](image-url)
RESULTS AND DISCUSSION

A drawback of regular RFO is the decrease of the NH\textsubscript{3} conversion. RFO with temporarily lower feed concentration is meant to overcome such conversion decrease. Moreover, RFO with temporarily lower feed concentration can also be used as a tool for the manipulation of the catalyst surface coverage, leading to a wide range of possibilities to increase the amount of desired product (see Figure 4-3). At this point, it should be clearly stated that the time period of lower feed concentration is the variable to focus on.

EFFECT OF TIME PERIOD OF LOWER FEED CONCENTRATION ON CONVERSION AND SELECTIVITY

Due to the limitation of the switching valves to operate the reactor at a switching time near to the gas residence time, the experiments for RFO with temporarily lower feed concentration were performed at a ratio $\alpha$ of switching time over gas residence time larger than 1. Following discussion deals with the experimental results for switching times of 5 s and 15 s, while the gas residence time is 0.6 s. The regime of the experiment at a switching time of 5 s is referred to as quasi-steady state regime, while the regime of the experiment at a switching time of 15 s is referred to as strongly quasi-steady state regime.

At switching time 5 s

The experiments to investigate the effect of time period of lower feed concentration on the conversion and selectivity were performed at switching time 5 s and the gas residence time 0.6 s. The inlet concentration of NH\textsubscript{3} was changed from 1 to 0 vol.% when the concentration programming was applied while keeping the inlet concentration of O\textsubscript{2} constant by using He as balance. The experimental results for the conversion of NH\textsubscript{3} and the selectivities to N\textsubscript{2}, NO, and N\textsubscript{2}O are presented in Figure 4-8. In general, the model is well able to describe the measured data.

The influence of the time period of lower feed concentration on the NH\textsubscript{3} conversion and the selectivities to N\textsubscript{2}, NO, and N\textsubscript{2}O is very significant. The conversion of NH\textsubscript{3} slightly goes up when increasing the time period of lower feed concentration. At longer $t_L$, the overall ratio of O\textsubscript{2} to NH\textsubscript{3} becomes larger. It causes an increased oxygen coverage, as explained later, which favours a larger conversion. At $t_L = 3.75$ s, the conversion of NH\textsubscript{3} in RFO with concentration programming reaches a higher value than in regular RFO and SSO. Apart from the increased oxygen coverage, the higher NH\textsubscript{3} conversion is also caused by feed stock saving. In regular RFO, a high concentration of
ammonia at the reactor entrance is flown out when reversing the flow direction. The corresponding conversion decrease is avoided by lowering the concentration of ammonia before switching the flow. Thus, both the concentration programming and the increased oxygen coverage enhance the conversion of NH$_3$.

The selectivities towards N$_2$ and N$_2$O decrease when $t_L$ increases, while the opposite situation holds for the selectivity towards NO. Compared to the steady state operation, the decrease of the selectivities to N$_2$ and N$_2$O may span from almost zero at regular RFO to around 15% at $t_L = 3.75$ s, while the increase of the selectivity to NO may be as high as 20%.

The selectivity manipulations depend predominantly on the availability of adsorbed oxygen on the catalyst surface (see Figure 4-9). In regular RFO, the oxygen coverage at the reactor outlet gradually decreases shortly after reversing the flow direction (see Figure 3-9), which might be slightly lower than in SSO. The opposite holds for RFO with concentration programming where the oxygen coverage is higher than in SSO as shown in Figure 4-9. This condition favours the selectivity to NO (Perez-Ramirez et al., 2004). The decrease of the ammonia concentration at the reactor inlet via concentration programming induces an increase of the oxygen coverage at all axial positions in the reactor.
At switching time 15 s

The experiments to investigate the effect of time period of lower feed concentration on the conversion and selectivity were also performed at a switching time of 15 s and a gas residence time of 0.6 s in order to observe the reactor performance at strongly quasi-steady state regime. The inlet concentration of NH$_3$ was again changed periodically from 1 vol.% to zero, while the inlet concentration of O$_2$ was kept constant by using He as balance. The experimental results for the conversion of NH$_3$ and the selectivities to N$_2$, NO, and N$_2$O are presented in Figure 4-10, together with model predictions. In general, the model is able to describe the observed trends of the data.

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**Figure 4-9.**
Model prediction of the oxygen coverage profile at discrete axial positions in the reactor as a function of time for SSO and RFO with concentration programming. T = 573 K, $\tau_0 = 0.6$ s, FR$_{SSO} = 1:1$, $t_s = 5$ s, and $t_L = 3.75$ s. The concentration of O$_2$ is 1 vol.%, while NH$_3$ changes from 1 vol.% to zero during RFO with concentration programming. TLFC denotes temporarily lower feed concentration.

**Figure 4-10.**
Effect of the time period of lower feed concentration on differences in conversion and selectivities between RFO and SSO (markers show experiments, thick lines show model predictions). T = 573 K, $\tau_0 = 0.6$ s, and $t_s = 15$ s. The concentration of O$_2$ is 1 vol.%, while NH$_3$ changes from 1 vol.% to zero during RFO with concentration programming.
The effect of the time period of lower feed concentration on the conversion of NH₃ and the selectivities to N₂, NO, and N₂O at a switching time of 15 s looks similar as observed at 5 s switching time. The observed differences, however, between RFO and SSO are smaller than in the case of 5 s switching time for both the ammonia conversion and the selectivities to all components. This should be expected for a larger switching time, as such condition provides a better approach of the quasi-steady state regime. Noteworthy is the point that a constant ratio \( t_L/t_s \) (time period of lower feed concentration over switching time) provides an equal time-average feed concentration. The observation that a smaller \( t_s \) at constant \( t_L/t_s \) provides larger differences between RFO and SSO means that the dynamics have a more important influence than the stoichiometry of the feed. Therefore, short switching times should be preferred in order to stimulate the conversion. A larger period of lower feed concentration can then be used to direct the selectivity towards more NO and less N₂ and N₂O. A too large \( t_L \) value at constant \( t_L/t_s \), however, would cause depletion of N containing species on the catalyst surface, leading to lower conversion (see Figure 4-3). Apparently, such situation was not met during the experiments shown in Figures 4-8 and 4-10.

EFFECT OF OXYGEN CONCENTRATION

The oxygen concentration has a large influence on both the activity and selectivity in the selective oxidation of ammonia. Increasing the oxygen feed concentration while keeping the ammonia concentration constant increases the activity, but the influence on the selectivity depends on the product type (Gang, 2002).

The effect of the oxygen concentration in the feed during RFO with concentration programming was studied experimentally. The data were obtained in the quasi-steady state regime (\( \tau_o = 0.6 \) s, \( t_s = 5 \) s, and \( t_L = 3.75 \) s). Three different oxygen concentrations were applied: 1, 2, and 3 vol.%. During concentration programming, the ammonia concentration was lowered from 1 to 0 vol.%. The oxygen concentration remains constant by adjusting the helium flow rate. Figure 4-11 shows the experimental results as the difference between RFO and SSO.

As shown in Figure 2-9 for SSO, the ammonia conversion attains a very high level, but there is a slight increase with more oxygen in the feed. The time-average conversion of NH₃ in RFO with concentration programming slightly decreases with increasing O₂ concentration (see Figure 4-11). The overall effect for the conversion difference between RFO and SSO therefore decreases at higher O₂ concentration. The model prediction slightly overestimates the experimental data. The model behaviour of the NH₃ conversion is in accordance with the minor changes of the oxygen coverage at the reactor outlet: 0.68 (at 1 vol.% O₂), 0.63 (at 2 vol.% O₂), and 0.73 (at 3 vol.% O₂),
respectively. The increase of the oxygen coverage at 3 vol.% O₂ in the feed may occur due to a shortage of N containing species after the NH₃ feed is stopped. The O₂ consumption cannot rise anymore and the oxygen coverage increases.

Increasing the inlet O₂ concentration coupled with the concentration programming of RFO strongly influences the product distributions, but in a completely different way as observed during SSO. As can be seen in Figure 4-11, the selectivity to N₂ is much lower than for SSO, especially at high oxygen concentration. The selectivities to NO and N₂O pass through a maximum and a minimum, respectively, while they show a gradual rise of 10% during SSO. Overall, the selectivity to NO is always considerably higher during RFO with concentration programming than in the case of SSO. The overall high NO and low N₂ level are caused by a higher oxygen coverage during RFO with concentration programming. The trend of lower N₂ selectivity with increasing oxygen content is in line with the SSO behaviour (see Figure 2-9a). The initially lower N₂O selectivity is remarkable and adds extra to the NO selectivity. A further increase of the oxygen content lowers the NO selectivity. This could be explained from a larger NO coverage, which favours N₂O formation.

**EFFECT OF TEMPERATURE**

The effect of temperature on ammonia conversion and product distribution in RFO with temporarily lower feed concentration is presented in Figure 4-12.
The conversion of ammonia gradually increases when the temperature increases. The model prediction slightly overestimates the experimental data. In principle, increasing the reaction temperature causes larger reaction rates, leading to a higher NH3 conversion. The increase of reaction temperature from 573 K to 673 K results in about 3% (model) and 1% (experiment) conversion increase. Such an increase is considerable in view of a steady state conversion, which has already reached a high level. The results are slightly below the SSO data. Compared to regular RFO at 673 K and \( t_s = 5 \text{ s} \), RFO with concentration programming results in a higher ammonia conversion of about 7%.

Increasing the reaction temperature in RFO with temporarily lower feed concentration induces distinct selectivity changes. Increasing the temperature decreases the selectivity to N2 much more than during SSO (see Figure 2-7). The selectivity to N2O passes a maximum during SSO but is now considerably lower. The selectivity to NO shows a large increase. In principle, the selectivity changes in RFO with temporarily lower feed concentration are in line with the steady state operation. The effect of concentration programming definitely gives rise to an increase of the oxygen coverage, which leads to much higher selectivity to NO.

EFFECT OF AMPLITUDE

The effect of the feed concentration of NH3 during RFO with concentration programming on the conversion and selectivity was investigated at a switching time of 5 s, a gas residence time of 0.6 s, and a time period of lower
feed concentration of 2.5 s. In this case, the inlet concentration of NH₃ was changed from 1 vol.% to zero (so called amplitude 1) or from 2 vol.% to zero (so called amplitude 2) when concentration programming was applied. The inlet concentration of O₂ was maintained constant at 1 vol.% by using He as balance. It is to be expected that the increase of NH₃ in the feed may influence the local catalyst coverage with N containing species, which affects the product distribution. Figure 4-13 compares the conversion and selectivities obtained in RFO with concentration programming to SSO for both amplitudes 1 and 2.

Decreased conversion is observed at higher inlet concentration of NH₃. This might be caused by a decrease of the oxygen coverage as a result of more N containing species. The latter is the major key for the increase of the selectivity to N₂. Since the oxygen coverage becomes less with more NH₃ in the feed, the selectivity to NO goes down, while the opposite holds for N₂O.

CONCLUDING REMARKS

It was shown that reverse flow operation with concentration programming of NH₃ while keeping the inlet concentration of O₂ constant might increase the oxygen coverage. Such increased oxygen coverage favours the selectivity to NO. The time period of lower feed concentration is a major key to manipulation of the product distributions. The productivity and the production rate were influenced as well. It was investigated experimentally and validated with the model that increasing the time period of lower feed concentration increases the conversion of NH₃ and the selectivity to NO while decreasing the selectivities to N₂ and N₂O. A higher oxygen concentration in the feed decreases the conversion of NH₃ and notably the selectivity to N₂. The rise of the NO selectivity is enormous at the expense of N₂O as well, but further increasing the oxygen content causes a partial shift from NO to N₂O.
higher temperature causes a slightly larger NH$_3$ conversion and a pronounced increase of the selectivity to NO, while the selectivities to N$_2$ and N$_2$O both decrease. An increased amplitude of NH$_3$ decreases the NH$_3$ conversion and selectivity to NO, while the opposite holds for the selectivities to N$_2$ and N$_2$O.
A novel concept of reverse flow operation (RFO) with reactor side feeding is studied for selective oxidation of NH₃ to produce either N₂, NO, or N₂O. This novel concept is proposed to avoid the conversion decrease during regular RFO. The production rate of the desired product can be kept at a high level, which may exceed the level of regular RFO and even of steady state operation (SSO). The reactor behaviour was studied for quasi-steady state, dynamic, and sliding regimes with varying feed positions. The development of spatio-temporal patterns inside the reactor with side feeding shows completely different behaviour compared to regular RFO and SSO, leading to the possibility of conversion and selectivity manipulations. The proposed concept also indicates a better conversion for the dynamic and sliding regimes. The influence of shifting the feed positions to the reactor center is most pronounced if the switching time is shorter. This concept also provides an opportunity to prevent the dead gas volume in the center of the reactor.
regular reverse flow operation (RFO) and a novel concept of RFO with temporarily lower feed concentration have been discussed in Chapters 3 and 4, respectively. It was aforementioned in Chapter 3 that an outflow of highly concentrated, unconverted reactant, shortly after reversing the flow direction will occur during regular RFO. As a consequence, the conversion is always lower when compared to steady state operation (SSO), while the product distributions do not change significantly. The operation technique was then modified by RFO with temporarily lower feed concentration as discussed in Chapter 4. This concept obviously seems promising to improve the reactor performance as indicated by an improved conversion and significantly different product distributions. However, RFO with temporarily lower feed concentration suffered from a pronounced decrease of the production rate. In Chapter 5, another novel concept of RFO with reactor side feeding is proposed to overcome this major drawback.

INTRODUCTION

Reverse flow operation with reactor side feeding has already been considered for trapping strongly adsorbing NH₃ species during the selective catalytic reduction of NO by NH₃ (Agar and Ruppel, 1988). Simulations showed that side stream NH₃ addition enables better mass trapping compared to addition from the reactor ends as well as better control of axial adsorbate profiles (Snyder and Subramaniam, 1998). A correlation was found between the reversal time to prevent the escape of adsorbing species and the concentration of non-adsorbing species. As a result, RFO with central introduction of adsorbing species could be more efficient than a conventional reverse flow operation (Falle et al., 1995). Reverse flow operation for NO reduction with central NH₃ introduction was also used for safety considerations in relation to ammonium salt formation on the catalyst (Noskov et. al., 1993; Mearns et al., 1984).

As the dynamics of RFO for manipulation of selectivity are much faster than their equivalents in the case of energy saving, it requires considerably more frequent flow reversals with a switching time in the same order of magnitude as the residence time is. This kind of operation induces a serious decrease of the conversion, which is mainly caused by an outflow of highly concentrated, unconverted reactant shortly after reversing the flow direction (see Figure 3-4, Chapter 3). This amount of gas actually had a shorter residence time and higher reactant concentration compared to the rest of the reactor’s gas hold-up. To overcome the conversion decrease at low switching time, a new concept of RFO with concentration programming as proposed by Budhi et al. (2003b, 2004a) seems very promising. By temporarily decreasing the feed concentration before reversing the flow direction, a better conversion can be obtained in the RFO compared to the steady state operation. Furthermore, the
selectivity can be manipulated freely in a significant range. However, this technique induces a considerable decrease of the production rate.

Another option to improve the conversion during reverse flow operation is considered here by applying the novel concept of reverse flow operation with reactor side feeding. In this application, the feed gas does not enter the reactor at $z = 0$ (forward) or $z = 1$ (backward) as in regular flow reversal, but at some axial coordinates in between. The reactor outlets still flow out from the usual positions at $z = 0$ or $z = 1$, depending on the flow direction. Figure 5-1 depicts the simplified flow diagram of RFO with reactor side feeding.

Such an approach might be feasible to avoid the conversion decrease because the gas with high reactant concentration, which entered the reactor shortly before the flow direction is changed, now still may contact the catalyst when flowing out of the reactor. Moreover, the ‘dead’ gas volume in the reactor center, which exists if the switching time between flow reversals is smaller than the residence time, could be possibly avoided as well when suitable feed positions are applied. These fundamental aspects are addressed in this chapter via reactor analysis, numerical simulation, reactor design, and laboratory experiments. Focus is on a comparison of reactor conversion and selectivity, obtained in a reverse flow operation with both regular feeding and side feeding, and also on comparison with steady state, once-through operation. Three kinds of regime were considered: the quasi-steady state regime, the dynamic regime, and the relaxed steady state regime during the simulations, while only the quasi-steady state regime was studied during the experiments due to limitations of the switching valves.

Figure 5-1.
Schematic diagram of RFO with reactor side feeding. The solid line shows where the feed gas flows into the reactor during the first half of each cycle, while the dashed line shows where the feed gas flows into the reactor during the second half of each cycle.
MODELING OF RFO WITH REACTOR SIDE FEEDING

In the reverse flow operation with reactor side feeding, the feeds are positioned at some axial coordinates in between the reactor ends. A symmetric switching time is usually applied, meaning that the periods of forward and backward flows are equal. Another crucial point of concern is the feed position, which might be designed in a symmetric or asymmetric way.

The working principle is fundamentally similar as in RFO operation. Therefore, the model equations of regular RFO as already shown in Table 2-1 can still be applied to reverse flow operation with reactor side feeding, except for some adaptations of the boundary conditions. Table 5-1 shows the adapted boundary conditions for reverse flow operation with reactor side feeding.

ANALYSIS OF RFO WITH REACTOR SIDE FEEDING

INTERRUPTED AND REVERSED FLOW REGIONS

Figure 5-2 shows the scheme of a reverse flow reactor with side feeding, defining the axial positions of the feeds and the distinct zones in the reactor. Feeds are positioned at axial coordinates $z = \frac{L_a}{L_r}$ and $z = 1 - \frac{L_a}{L_r}$ in terms of dimensionless reactor length. The regions $0 \leq z \leq \frac{L_a}{L_r}$ and $1 - \frac{L_a}{L_r} \leq z \leq 1$ are referred to as ‘interrupted flow regions’, where the flow is alternately stopped or in one direction only. In the ‘reversed flow region’, $\frac{L_a}{L_r} < z < 1 - \frac{L_a}{L_r}$, the flow direction is periodically alternated.

<table>
<thead>
<tr>
<th>Table 5-1. Boundary conditions for RFO with reactor side feeding.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundary conditions, $t &gt; 0$:</td>
</tr>
<tr>
<td>Forward flow</td>
</tr>
<tr>
<td>$\left. \frac{\partial p_i}{\partial z} \right</td>
</tr>
<tr>
<td>Backward flow</td>
</tr>
<tr>
<td>$\left. \frac{\partial p_i}{\partial z} \right</td>
</tr>
</tbody>
</table>
In the regions of the interrupted flow, unconverted reactant that just entered into the reactor still comes into contact with the catalyst after reversal of the flow direction. Moreover, whenever the flow is interrupted, these regions act as a batch reactor, which adds an extra contribution to the conversion. Because the feed gas introduction from the reactor side can affect the dynamics of the catalyst surface coverage, possible selectivity manipulation is of great interest.

**AVOIDING DEAD GAS VOLUME**

In the quasi-steady state and dynamic regimes of regular RFO, the switching time is larger than the gas residence time. It means that between subsequent flow reversals, the gas volume of the fixed bed is flown through completely, and a dead gas volume is not present.

In the relaxed steady state regime, however, the switching time is smaller than the gas residence time. As a result, the gas volume in the central part of the reactor is not flown through anymore between flow reversals. Although the actual conversion in this dead volume is high in itself and may even reach full conversion, it does not contribute to the overall reactor conversion. In fact, regular reverse flow operation in this situation causes a decrease of the overall reactor conversion due to ineffective use of catalyst.

A flushing method, i.e. alternation between RFO and once-through operation, may improve the reactor conversion, but values as would be obtained in once-through SSO still cannot be reached (Budhi et al., 2003b). In the RFO with reactor side feeding, it is possible to avoid such a dead gas volume if a suitable switching time at fixed feed positions is applied. Therefore, the ineffective use of the catalyst can be avoided accordingly.

The dead gas volume in the reactor can be prevented if the region between the two feed points (at \( L_a \) and at \( L_r - L_a \)), with a length:

\[
L_{\text{min}} = L_r - 2L_a
\]  \hspace{1cm} (5-2)
is completely flown through during the switching time. The minimum time required to pass this ‘reversed flow region’ is defined as the minimum switching time ($t_{s,min}$) and can be written as:

$$t_{s,min} = \varepsilon_b \frac{(L_r - 2L_a)}{u_s} \quad (5-3)$$

with $L_r$ the total reactor length and $u_s$ the superficial velocity.

With the definition of the residence time for once-through operation $\tau_o = \varepsilon_b L_r / u_s$, Equation 5-3 is rewritten as:

$$t_{s,min} = \tau_o \left( 1 - 2 \frac{L_a}{L_r} \right) \quad (5-4)$$

**RESIDENCE TIME DISTRIBUTION**

Reverse flow operation with reactor side feeding invokes a unique and peculiar behaviour. It can be well understood from the residence time distribution, associated with this operation concept. The residence time distribution of RFO with side feeding is of interest to obtain insight in the achievements of this type of operation. It will be considered here for situations that the switching time is equal to the minimum switching time.

**Case $L_a = L_r/3$**

The minimum switching time equals $\tau_o/3$ according to Equation 5-4. The minimum residence time $\tau_{min}$ basically has two contributions: one from flowing through an interrupted flow region and another from standing in this region, while flow is through the other interrupted flow region. So $\tau_{min}$ equals $2\tau_o/3$. The maximum residence time $\tau_{max}$ has additional contributions from flowing through the reversed flow region in forward and backward direction. Each of them being $\tau_o/3$, the maximum residence time is $4\tau_o/3$. In between $\tau_{min}$ and $\tau_{max}$, the distribution is uniform as shown in Figure 5-3. The average residence time equals $\tau_o$ as it should do.

**Case $0 < L_a < L_r/3$**

In this case, the minimum switching time is always larger than $\tau_o/3$. The minimum residence time equals the residence time in the interrupted flow region:
\[
\tau_{\text{min}} = \frac{\varepsilon b L_a}{u_s} = \frac{\tau_o L_a}{L_r} \tag{5-5}
\]

The reversed flow region adds in between 0 and \(2t_{s,\text{min}}\) to this minimum residence time, but part of the gas stands an extra time \(t_{s,\text{min}}\) in the interrupted flow region. This part concerns the fraction \(L_a/(L_r - 2L_a)\) of the gas in the reversed flow region and has residence times in between \(3t_{s,\text{min}} - \tau_{\text{min}}\) and \(3t_{s,\text{min}} + \tau_{\text{min}}\). The latter is also the maximum value of the residence time, which consists of contributions from flowing up and down the reversed flow region plus flowing and standing in the interrupted flow region. So in this case the residence time distribution is bimodal. For small values of \(L_a/L_r\), there exists a small amount of gas with a considerably larger residence time. With increasing \(L_a/L_r\), the two parts of the distribution function approach each other till they merge at \(L_a/L_r = 1/3\) (see Figure 5-3). Since the average residence time should be equal to \(\tau_o\), the value of the uniform distribution can be obtained from normalization.

**Case \(L_a/3 < L_a < L_r/2\)**

The minimum switching time \(t_{s,\text{min}}\) is now smaller than \(\tau_o/3\), meaning that all gas coming from the reversed flow region will stand in the interrupted flow region. The residence time distribution during RFO with reactor side feeding. The case \(L_a = L_r/3\) is shown as drawn lines, while the case \(0 < L_a < L_r/3\) is shown for \(L_a = L_r/10\) (— — —) and for \(L_a = L_r/5\) (- - -).
region for at least one minimum switching time. The value of \( \delta = \text{int}[L_a/(L_r-2L_a)] \) determines how many times the gas flow will be interrupted for \( t_{s,\text{min}} \) seconds, when the gas passes the interrupted flow region. The minimum residence time \( \tau_{\text{min}} \) is \( \delta t_{s,\text{min}} + \epsilon_b L_a/u_o \), which is equal to \( \delta t_{s,\text{min}} + \tau_o L_a/L_r \). The maximum residence time \( \tau_{\text{max}} \) is \( 2t_{s,\text{min}} \) larger, which accounts for forward and backward flows through the reversed flow region. If \( L_a/(L_r-2L_a) \) is an integer, the distribution of residence times is uniform between \( \tau_{\text{min}} \) and \( \tau_{\text{max}} \), i.e. it has a width of \( 2t_{s,\text{min}} \). If \( L_a/(L_r-2L_a) \) is not an integer, the residence time distribution becomes bimodal because part of the gas stands an extra time \( t_{s,\text{min}} \) in the interrupted flow region. Whether or not \( L_a/(L_r-2L_a) \) is integer becomes irrelevant if \( L_a \) approaches \( L_r/2 \) meaning that the minimum switching time decreases to zero. For sufficiently large values of \( \delta \), the residence time distribution is uniform between \( \tau_o - t_{s,\text{min}} \) and \( \tau_o + t_{s,\text{min}} \) with an average value of \( \tau_o \). The limit situation of \( L_a \) approaching \( L_r/2 \) corresponds with half of the flow rate moving from the middle of the reactor to one side, while the other half moves to the other side. This situation shows a residence time distribution, which is exactly the same as met with once-through operation.

For first order reactions the conversion is fully determined by the residence time distribution. This means that side feeding around \( L_a = L_r/3 \) provides opportunities to influence the conversion in a positive way because of the bimodal character of the distribution function. Part of the gas resides longer in the reactor, while another part has a shorter residence time. For reaction orders different from 1, the reaction kinetics have an influence as well. It is obvious that the reactor selectivity will be affected accordingly.

**SIMULATION RESULTS**

Simulation results of reverse flow operation with reactor side feeding are presented. First, its behaviour at different regimes is discussed and compared to the behaviour of regular reverse flow operation. Second, the effect of the feed position on conversion and selectivity is presented. Third, the conversion and selectivity under conditions of minimum switching time is demonstrated. All simulation results refer to a temperature of 800 K.

**BEHAVIOUR OF RFO WITH REACTOR SIDE FEEDING**

The simulation of regular reverse flow operation is used as a reference for the comparison to reverse flow operation with reactor side feeding. Figure 5-4 shows typical results of the ammonia partial pressure as a function of time for three different regimes during one complete cycle. Each regime is represented by a characteristic switching time. Regular reverse flow operation with the feed position at the outer ends of the reactor \((z = 0 \text{ or } z = 1)\) depending on the
flow direction) is shown in Figures 5-4a, c, and e. For reactor side feeding with feeds at \( z = 0.1 \) and 0.9, Figures 5-4b, d, and f, provide results at similar conditions. Operating conditions were mentioned in Table 2-4.

In the quasi-steady state regime \((\tau_0 = 10 \, \text{s}, \, t_s = 15 \, \text{s})\), the outlet concentration during regular reverse flow operation (Figure 5-4a) is able to reach the steady state value as shown by the horizontal part of the profiles. A short while after reversing the flow direction, the outlet concentration of ammonia is high because the high concentration of ammonia that just entered into the reactor is flown out again. This typical behaviour causes the decrease of conversion. In general, the time-average behaviour is not so different from the steady state performance. When reactor side feeding is applied (see Figure 5-4b), the concentration profiles in between the inactive inlet point and outlet point are also able to reach the steady state, while the concentration profiles in regions where flow is interrupted stay in the unsteady state due to continuing reaction. These patterns are clearly shown in Figure 5-4b. During the first half cycle \((130 \, \text{s} \leq t \leq 145 \, \text{s})\), the gas enters the reactor at \( z = 0.9 \), while the products leave the reactor at \( z = 0 \). The ammonia partial pressures at \( z = 0.1 \) and 0 reach the steady state value, while at the closed outlet, \( z = 1 \), the partial pressure continues to decrease. Such typical profiles are repeated during the next half cycle, which means the periodic flow reversal has already attained stable oscillations.

The behaviour in the dynamic regime \((\tau_0 = 10 \, \text{s}, \, t_s = 10 \, \text{s})\) seems similar to the quasi-steady state behaviour, apart for the constant steady state values, which do not exist. Before the profile can take steady state values, the reactor is perturbed again by flow reversal. In this way, the reactor is always maintained under dynamic conditions as shown by Figure 5-4c. Time-average behaviour is therefore to be expected as different from the steady state performance. When reactor side feeding is applied (see Figure 5-4d), similar behaviour is observed. Just after reversing the flow direction, the outlet concentration profile changes non-monotonously as a function of time without reaching the steady state. In reverse flow operation with reactor side feeding, the outlet concentrations are slightly higher for the dynamic regime (see Figure 5-4d) compared to the quasi-steady state regime (see Figure 5-4b). It is caused by the faster switching time in the dynamic regime. It also means that the period of interrupted flow is shorter in the dynamic regime than in the quasi-steady state regime, as reflected by less decay of reactant at positions in the interrupted flow region.
Figure 5-4.
Comparison of regular RFO (a,c,e) and RFO with reactor side feeding (b,d,f) for different regimes. The partial pressure of NH₃ is shown at various axial positions during one full cycle. For RFO with reactor side feeding, feed positions are at 0.1 and 0.9 in dimensionless reactor length. Bold arrows indicate the flow direction.
In the relaxed steady state regime \((\tau_0 = 10 \text{ s}, t_s = 2 \text{ s})\) for regular RFO, the concentration profiles look completely different (see Figure 5-4e). All profiles remain in the unsteady state and depend strongly on the ratio of switching time over residence time. Compared to the other two regimes, the outlet concentration in the relaxed steady state regime is much higher. When reactor side feeding is applied, see Figure 5-4f, the concentration levels in the relaxed steady state regime are also higher than in the other regimes. It should be emphasized, however, that Figure 5-4 refers to RFR with the feed positions at \(z = 0.1\) and \(0.9\), and that the opposite holds for feeds in the region \(0.3 < z < 0.7\). Such conditions lead to a lower outlet concentration, hence higher conversion.

Figure 5-5 shows the partial pressure of \(\text{NH}_3\) in the RFO with reactor side feeding during one full cycle for the quasi-steady state regime \((t_s = 15 \text{ s})\) and the relaxed steady state regime \((t_s = 2 \text{ s})\). The feed positions are placed more to the center, viz. at \(z = 0.4\) and \(0.6\). In the quasi-steady state regime, shifting the feed position toward the reactor’s center causes a higher concentration of \(\text{NH}_3\) in the interrupted flow region if flown through, while the concentration decay is similar if not flown through (compare Figures 5-4b and 5-5a). On the other hand, in the relaxed steady state regime, the outlet concentration of \(\text{NH}_3\) with feed positions 0.4 and 0.6 is definitely lower than with feed positions 0.1 and 0.9 (compare Figure 5-4f and Figure 5-5b). In the relaxed steady state regime with the same switching time, such low outlet concentration of \(\text{NH}_3\) is never reached by regular RFO. Figure 5-5b also shows that during the whole cycle the outlet concentration of \(\text{NH}_3\) in the relaxed steady state regime is lower compared to the outlet concentration of \(\text{NH}_3\) in the quasi-steady state regime (see Figure 5-5a).

**Figure 5-5.**
Partial pressure of \(\text{NH}_3\) as a function of time at discrete positions in the reactor during one full cycle. The feed positions are at \(z = 0.4\) and \(0.6\). The flow directions are shown by bold arrows. \(\tau_0 = 10 \text{ s}\). Other operating conditions are mentioned in Table 2-4. (a) quasi-steady state regime \((t_s = 15 \text{ s})\), (b) relaxed steady state regime \((t_s = 2\).
MOVING CONCENTRATION FRONT

Figure 5-6 provides a typical example of the ammonia partial pressure as a function of reactor length at discrete times in the dynamic regime ($\tau_0 = 10$ s, $t_s = 10$ s) during reverse flow operation with reactor side feeding. The curve at $t = 130$ s is the final profile of the previous half-cycle just before reversing the flow direction. The peak value of this profile expresses the feed gas concentration at $z = 0.9$, while the reactor outlet is at $z = 0$. When the flow direction is now reversed, the inlet gas is fed at $z = 0.1$ and the reactor outlet is at $z = 1$. The steep gradient at $z = 0.1 – 0.2$ becomes less steep while moving through the reactor over time (131, 132, 133, 135 s). At $140$ s the profile’s shape is a mirror image of the profile at $130$ s. A lower minimum at $t = 135$ s compared to $t = 133$ s is caused by the ongoing reaction. The profile at $130$ s in the region 1 to 0.9 indicates that the outlet concentration at $z = 1.0$ first will rise and then decline when the region from 0.9 to 0.5 reaches the outlet. Finally, the concentration at $z = 1$ rises again if the minimum value (see profiles at 133 and 135 s) has passed the outlet. It produces the concentration versus time behaviour at the reactor outlet ($z = 1$) as shown in Figure 5-4d.

EFFECT OF FEED POSITION ON CONVERSION AND SELECTIVITY

Figure 5-7 shows time-average values of the conversion of NH$_3$ and the selectivities toward N$_2$, NO, and N$_2$O as a function of the feed position at different switching times, which reflect the various operation regimes. In general, there are two effects that have an influence on the reactor conversion when shifting the feed positions to the reactor center.

![Figure 5-6.](image)
Gas phase NH$_3$ profile along the reactor length at discrete times during one half-cycle. $t_s = 10$ s, $\tau_0 = 10$ s, and feed positions are at $z = 0.1$ and 0.9. Other conditions as mentioned in Table 2-4.
• The volume of the interrupted flow region increases, which causes a higher conversion due to longer gas residence time and less outflow of unreacted gas shortly after a flow reversal.

• The volume of the rest of the reactor decreases, which lowers the conversion obtained in this part.

The overall behaviour is rather complicated because of the interaction of these effects. In the quasi-steady state (see Figure 5-7a, curve 15 s), the conversion of ammonia slightly decreases non-monotonously when the feed positions are shifted to the reactor center. The behaviour in the dynamic regime (Figure 5-7a, curve 10 s) looks similar as in the quasi-steady state, but the general trend is now increasing. The influence of the feed position in the quasi-steady and dynamic regimes is not impressing, contrary to the effects in the relaxed steady state regime. Here, two different switching times of 5 and 2 s were applied. In both cases, the conversion of ammonia shows a large increase when the feed positions are shifted to the reactor center. The effect is most pronounced if the switching time becomes shorter, probably because of the increasing amount of flow interruptions in the interrupted flow region.

Reverse flow operation with reactor side feeding also affects the selectivity of the products. Although the conversion level itself has an influence on the selectivity, the differences in product distributions result from reverse flow operation as shown by a comparison to the steady state at constant conversion (Budhi et al., 2004b). Figures 5-7b, c, and d show the effect of reactor side feeding on the selectivity. The selectivity to N₂ increases slightly in the quasi-steady and dynamic regimes if the feed positions shift to the reactor center. It decreases, however, significantly in the relaxed steady state regime, at high flow reversal frequency. The selectivity to N₂O also decreases considerably in the relaxed steady state regime, while the feed position hardly has an influence in the other regimes. Similarly, the selectivity to NO shows minor changes in the quasi-steady and dynamic regimes if the feed positions shift to the reactor center, but the NO selectivity increases considerably in the relaxed steady state regime. Therefore, the application of reverse flow operation with reactor side feeding may have an important positive effect on the conversion and the selectivity if NO is the desired product, and production of N₂O and N₂ should be avoided.
Figure 5-7.
Time-average conversion of NH₃ and time-average selectivities to N₂, N₂O, and NO as a function of the feed position in terms of dimensionless reactor length at different switching times. $\tau_o = 10$ s. Other operating conditions as mentioned in Table 2-4. Values at feed position zero refer to regular RFO. Steady state values are: conversion of NH₃ is 87.5%, selectivity to N₂ is 14.6%, selectivity to NO is 78.1%, and selectivity to N₂O is 7.3%.

CONVERSION AND SELECTIVITY AT MINIMUM SWITCHING TIME

For conditions of minimum switching time for each chosen feed position, Figure 5-8 shows the conversion of NH₃ and the selectivities to N₂, NO, and N₂O as a function of the dimensionless feed position for one-half of the reactor
so this figure shows the locus of conversion and selectivity at the minimum switching time. Feed positions and the minimum switching time in Figure 5-8 relate to each other as shown via the bottom and top axis. All minimum switching times applied in Figure 5-8 relate to the relaxed steady state regime, which seems most interesting (see Figure 5-7). The reactor performance in the RFO with side feeding is better than during regular RFO and even steady state, once-through operation, particularly when the feed positions are near to the reactor center. The conversion and selectivities during regular RFO at similar conditions are actually the values at the feed position $z = 0$ in Figure 5-8, while steady state values are indicated by marks on both axes.

**EFFECT OF SIDE FEEDING ON ADSORBED OXYGEN**

Figure 5-9 shows how the oxygen surface coverage changes over one cycle at different axial positions during RFO with reactor side feeding at $z = 0.03$ and 0.97. The conversion of NH$_3$ increases if the feed positions are shifted to the reactor centre. The increase of the NH$_3$ conversion boosts up if the feed positions exceed $L_a/L_r = 0.3$ (see Figure 5-8). Simultaneously the selectivities of N$_2$ and N$_2$O decrease significantly, but the selectivity of NO increases. Apparently, the distribution of residence times for $L_a/L_r > 0.3$ is beneficial for ammonia conversion and NO production. This is due to the abundance of adsorbed oxygen on the catalyst surface coverage (see Figure 5-9b), which favours both conversion and NO formation. It is obvious that side feeding induces coverages of 0.7 and more, while they are 0.6 or periodically much less during regular RFO (Figure 5-9a). It is shown that reactor side feeding provides a way to overcome most of the conversion decrease, met during regular RFO, while clearly different selectivities can be obtained.

![Figure 5-8](image.png)

*Figure 5-8.* The conversion and selectivity at minimum switching time for RFO with reactor side feeding. Operating conditions, see Table 2-4. $\tau_o = 10$ s. Feed position 0 corresponds with regular RFO. Markers show steady state: ○ conversion of NH$_3$, □ selectivity to N$_2$, ○ selectivity to NO, ■ selectivity to N$_2$O.
CHAPTER 5. Reverse Flow Operation with Reactor Side Feeding

EXPERIMENTS

NEW REACTOR DEVELOPMENT

A new reverse flow reactor was designed with emphasis on side feeding features. Figure 5-10 shows a cross-section (a), an isometric view (b), and a schematic representation (c) of the reactor. The design accounted for side feeding at two distinct positions: either at $z = 0.2$ and 0.8 or at $z = 0.4$ and 0.6 in terms of dimensionless axial coordinates. The latter situation is shown in Figure 5-10 and described below.

Major parts are 5 compartment rings and 2 reactor heads (see Figure 5-10b). Each ring has a peripheral channel. For rings 1 and 5, this channel is connected with 8 axial channels in parallel in the wall of the ring, which traverse the whole height of the ring. The feed lines, connected to either head H1 or H2, end up in the peripheral channel, which allows the feed to pass compartment 1 or 5 through the wall. Rings 2 and 4 are similar, but the axial channels do not traverse the ring’s height completely. Now they end up at a quartz sintered plate, which covers up the whole cross-section of the reactor. Via the radial channel in the sintered plate, the feed is evenly distributed over
the cross-section and enters the catalyst bed. The reactor outflow occurs through the center of the other head.

![Diagram of reactor](image)

**Figure 5-10.** Visualization of the reverse flow reactor with side feeding, showing 5 compartments and 4 sintered quartz plates: (a). reactor cross section along the axial direction, (b). isometric view, (c). feed gas mechanism when entering into the reactor, white and black valves indicate open and closed positions, respectively.

The catalyst mass is divided in three portions, kept apart by four sintered plates (Figure 5-10). Two plates act as feed distributors, while the other two are positioned at the outlets to keep the catalyst inside the bed.

By exchanging rings 1 and 2, as well as rings 4 and 5, the feed positions become located at \( z = 0.2 \) and 0.8. Three thermocouples at fixed positions allow to monitor the axial temperature profile. Gas sampling occurs at two inlet and two outlet positions via capillaries, in which each of them can be directed to the mass spectrometer. As described in Chapter 2, reactor heating was carried out again with a fluidized sand bath. Contrary to Chapter 2, the reactor was now positioned vertically because of the sand-bath dimensions.

### CATALYST LOADING

The catalyst used in this work is the same as used in the experiments of previous chapters. For RFO with side feeding, the catalyst loading was performed progressively for each compartment using a special holder. After the first compartment was fully filled with the catalyst, the second
compartment was put on top of it, filled, and so on. The sintered plates were symmetrically installed either at \( z = 0.2 \) and 0.8 or at \( z = 0.4 \) and 0.6, depending on the applied feed positions. Once the reactor was completely filled with catalyst, all reactor pieces were tightly kept together by applying threaded rods. Then the reactor was mounted in the set-up and carefully checked for possible leakages. Catalyst activation was subsequently carried out as described in Chapter 2.

RESULTS AND DISCUSSION

The variables, studied during RFO with reactor side feeding, include the switching time, temperature, and feed position. A gas residence time \( \tau_o = 0.6 \text{ s} \) was applied, while switching times varied from 2 to 10 s. It means that all experiments were carried out in the quasi-steady state regime. A typical transient profile as observed during RFO with reactor side feeding will be discussed first.

TRANSIENT PROFILE

Figure 5-11 shows the periodic profiles of the \( \text{NH}_3 \) concentration during RFO with reactor side feeding. The feed gas enters the reactor at \( z = 0.4 \) or \( z = 0.6 \), depending on the flow direction. In this case, the gas volumetric flowrate was 5000 nml/h, which corresponds to 0.6 s of the gas residence time in once-through operation. The switching time was 10 s. The minimum switching time to prevent a dead gas volume would be 0.12 s. The time periods of 10 – 20 s and 30 – 40 s indicate the observation using an online mass spectrometer when the gas is flowing through, while the time period of 20 – 30 s is the observation when the flow interrupted. The gas sampling was taken from a fixed point of the reactor outlet.

Figure 5-11. Concentration profiles of \( \text{NH}_3 \) over time for RFO with reactor side feeding. Conditions: \( T = 573 \text{ K}, \tau_o = 0.6 \text{ s}, t_s = 10 \text{ s}, \text{ FR} = 1:1, \) and feed positions at \( z = 0.4 \) and 0.6. Markers: experiments, curves: model predictions.
As can be seen in Figure 5-11, the observed concentration of NH$_3$ is higher when the gas is flowing through compared when the gas is interrupted. When the gas is flowing through the reactor with the feed position at $z = 0.4$ or $0.6$, the dimensionless length of the catalyst bed from the feed position to the reactor outlet is only $0.6$. It induces the conversion drop accordingly. In the interrupted flow region, the lower observed concentration is caused by the ongoing reaction as in a batch reactor during one-half cycle.

**EFFECT OF SWITCHING TIME**

Figure 5-12 shows the experimental results of RFO with reactor side feeding when the switching time is varied, while the feed positions are fixed. The markers in the figure show the experimental results, while the thick solid lines show the model predictions. The experimental conditions are as follows: $T = 573$ K, $\tau_0 = 0.6$ s, $FR = 1:1$, and $z_a = 0.4$ or $0.6$.

The conversion of NH$_3$ and the selectivities to N$_2$, NO, and N$_2$O were calculated as time-average values. Results are shown again in comparison to steady state operation. The change of conversion of NH$_3$ decreases when increasing switching time. One would expect, at first glance, that the conversion at large switching time would correspond most of all with the quasi-steady state, e.g. would yield the same result as observed during steady state. It should be realized, however, that during reverse flow operation with
side feeding at 0.4 and 0.6 just 60% of the catalyst mass in flown through in comparison to steady state operation. Notably at larger switching times, the interrupted flow region hardly contributes to the conversion as here reaction does not occur due to a lack of reactants. The latter is confirmed by Figure 5-11, which shows that NH₃ conversion in the interrupted flow region occurs only shortly after the flow has stopped. So for large switching times, Figure 5-12 should indeed indicate a decrease of conversion when comparing reverse flow operation plus side feeding to steady state operation, which decrease in related to a different real contact time (0.6 s for SSO, 0.48 s for RFO plus side feeding). At shorter switching time, the interrupted flow region contributes significantly to the conversion, as reflected by the sharp concentration decay just after stopping to the flow. Therefore, data points at short switching time in Figure 5-12 show higher conversion than those at large switching time. The model predictions show a small increase at short switching time. As shown in Figures 5-7 and 5-8, the influence of the feed position is indeed minor in the quasi-steady state regime, but more significant if real short switching times could be applied.

The selectivity changes for N₂ and NO decrease with increasing switching time, as shown in Figure 5-12, while they increase for N₂O. For all conditions in Figure 5-12, the selectivities to N₂ and NO are lower compared to steady state operation, while it is higher for N₂O. The effects are more pronounced if the switching time is larger. Model predictions do not expect an influence of the switching time in the quasi-steady state regime (see also Figures 5-7 and 5-8), which is remarkable. The selectivity results at large switching time can be explained, as previously for the conversion, by the fact that only 60% of the catalyst mass plays an active role in the process. As shown in Figure 2-11 for steady state operation, a small decrease of the residence time in the range of 0.6 to 0.5 s favours a higher N₂O selectivity and lower selectivities to N₂ and NO, which is inline with the selectivity differences between RFO and SSO in Figure 5-12. At short switching times, the differences become smaller due to the contribution of the interrupted flow region. Figure 5-13 illustrates this point by showing O and N coverages at the reactor outlets z = 0 and z = 1 for short and long switching times. Figure 5-13 indicates a high O and N coverages if the interrupted flow region is flown through. But if not flown through, Figure 5-13a shows a strong decay of the N coverage if the switching time is short, while the N coverage is zero most of time if the switching time is large. The latter indicates a shortage of N species due to full conversion in the interrupted flow region.
Figure 5-13. Oxygen and nitrogen coverages in RFO with reactor side feeding as predicted at the reactor outlet. The switching times are 2 s (a) and 10 s (b). Solid line shows coverage at $z = 0$. Dotted line shows coverage at $z = 1$. Arrows show the flow direction. Other conditions as mentioned in Figure 5-12.

Figure 5-14 shows similar profiles and conditions as Figure 5-12, but at feed positions $z = 0.2$ and 0.8, depending on the flow direction. In comparison to Figure 5-12, all differences between RFO plus side feeding and SSO are much smaller, which is caused by two effects. First, instead of 60% catalyst mass, now 80% is actively flown through, which causes zero differences between RFO and SSO at large switching times. Second, the amount of catalyst in the interrupted flow region is smaller, which lowers the contribution of this part of the reactor also at short switching times. The selectivity changes as function of the switching time show similar trends as observed in Figure 5-12. Model predictions for the conditions of Figure 5-14 are much better than for those of Figure 5-12 with feeds more to the center of the reactor. This could be caused by the fact that the conditions of Figure 5-14 better approach regular RFO. For regular RFO (Figures 3-8 and 3-9), experimental data and model predictions also showed a good agreement of trends.

EFFECT OF RESIDENCE TIME

The effect of gas residence time on the conversion of NH$_3$ and the selectivities to N$_2$, NO, and N$_2$O in RFO with reactor side feeding is shown in Figure 5-15. The gas is fed into the reactor at $z = 0.4$ or 0.6, depending on the flow direction. The markers in the figure show the experimental results, while the thick solid lines show the model predictions.
The changes of the conversion of NH$_3$ decrease with increasing gas residence time when comparing RFO with side feeding with SSO. The explanation for observed conversion effects in Figure 5-15 is similar as for the results in Figure 5-12. For a fixed switching time of 2 s, a short residence time of 0.3 s means
that the experiment is performed at conditions relatively close to the quasi-
steady state. Therefore, the involvement of only 60% of the catalyst mass
during RFO with side feeding has a large and negative influence on the
conversion level. At a large residence time of 0.9 s, however, conditions move
away from the quasi-steady state regime, and the interrupted flow region has
a positive effect on the conversion. The same was seen in Figure 5-12 for short
switching time. Model predictions confirm the observed trend of the NH₃
conversion in Figure 5-15. Model predictions are also in agreement with the
observed trends for changes of the selectivities to N₂, NO, and N₂O. At a
residence time of 0.6 s, which was applied for most experiments in this
chapter, the differences between RFO plus side feeding and SSO are the
smallest.

EFFECT OF TEMPERATURE

The effects of temperature on the conversion and selectivities were also
measured during the experiments of RFO with reactor side feeding. The
experimental results and the model predictions are shown in Figure 5-16. The
model predictions can describe the experimental results quite well.

During steady state operation, a temperature increase gives rise to a slightly
higher conversion of NH₃, see Figure 2-7b. In RFO with reactor side feeding,
the conversion of NH₃ decreases considerably with increasing temperature.
Therefore, the conversion difference between RFO with reactor side feeding
and SSO becomes larger when increasing the temperature (see Figure 5-16). At higher temperature, reaction rates become larger. This may cause a full conversion of NH$_3$ in the interrupted flow regions as a relatively large switching time depletes N species on the catalyst surface. The amount of active catalyst for converting NH$_3$ is then only 60% of the amount of catalyst present during SSO. This effect would be avoided when shorter switching times could have been applied.

The selectivity to N$_2$ decreases when increasing the temperature, both for SSO and for RFO with reactor side feeding. However, the decrease of the selectivity to N$_2$ during RFO with reactor side feeding is more pronounced at high temperature, which is reflected by negative value in Figure 5-16. RFO with reactor side feeding favours a larger the selectivity to N$_2$ at low temperature. Both during SSO and RFO with reactor side feeding, the selectivity to NO increases when the temperature increases. The absolute difference between RFO with reactor side feeding and SSO results in a selectivity increase up to a maximum, followed by a selectivity decrease (see Figure 5-16). The influence of the temperature on the selectivity to N$_2$O indicates a similar trend both for SSO and for RFO with reactor side feeding, i.e. it increases up to maximum, followed by a decrease with a further increase of the temperature. The absolute difference between RFO with reactor side feeding and SSO shows that the selectivity to N$_2$O in RFO with reactor side feeding is higher than in SSO at high temperature, while it is lower at low temperature. The overall result is that, compared to SSO, RFO with side feeding favours N$_2$ at low temperature and N$_2$O at high temperature.

When the feed positions are placed more near to the reactor centre, while the switching time is larger than the gas residence time, the actual gas residence time from the feed position to the reactor outlet becomes shorter. At high temperature, the consumption of NH$_3$ takes place much faster. When NH$_3$ has been fully converted in the interrupted flow region, the production rates of N$_2$, NO, and N$_2$O in that region stop accordingly. Now, the shorter catalyst bed in between the feed position and the reactor outlet affects strongly the selectivity next to the influence of the temperature. The shorter actual gas residence time increases the selectivity to N$_2$O and decreases the selectivities to N$_2$ and NO.

**EFFECT OF FEED POSITION**

The effect of the feed position on the conversion and selectivities was measured as well during experiments of RFO with reactor side feeding. The feed positions were chosen at $z_a = 0.2$ and 0.8, and at $z_a = 0.4$ and 0.6. The experimental results and the model predictions are shown in Figure 5-17. The operating conditions are as follows: $T = 573$ K, $t_s = 2$ s, $FR = 1:1$, and $\tau_o = 0.6$ s.
The changes of the conversion of NH\(_3\) slightly decrease when the feed positions are shifted more to the reactor center. This is inline with the model predictions as shown for the quasi-steady state regime in Figure 5-7a \((t_s = 15\) s\). Selectivity changes for the quasi-steady state conditions of Figure 5-17 are minor as they are for model predictions in Figures 5-7b to 5-7d. The observations for NO and N\(_2\)O seem to follow the predicted trends, while N\(_2\) does not. It is clear that shorter switching times are required to observe the large influences as predicted by Figures 5-7 and 5-8.

**CONCLUDING REMARKS**

At larger ratio of the switching time to the gas residence time and when the feed positions are more near to the reactor center, the conversion of NH\(_3\) and the selectivities to N\(_2\) and NO decrease, while the selectivity to N\(_2\)O increases. Increasing the gas residence time increases the conversion of NH\(_3\). The product distributions of N\(_2\) and N\(_2\)O show a minimum value, while a maximum exists for NO. At \(T = 573\) K, the selectivity to NO during RFO with reactor side feeding is always lower than for SSO, while the opposite holds for the selectivity to N\(_2\)O. The selectivity to N\(_2\) changes around zero. A temperature increase apparently decreases the conversion of NH\(_3\) and the selectivity to NO and N\(_2\)O increase. Although all experiments were carried out in the quasi-steady state regime, it became clear that a stronger influence of side feeding can be expected if the ratio of
switching time over residence time is smaller. This behaviour is ascribed to the contribution of the interrupted flow regions. These regions add only to conversion and selectivity shortly after the flow is stopped, i.e. as long as reactants are present. RFO with side feeding gives opportunities to attain product distributions that deviate from steady state results.
The discovery of reverse flow operation (RFO) and its successful application is a typical example of the development of reactor technology, which has led to a breakthrough in process intensification. Since then, RFO diversified and grew up in a spectacular way through the generation of new processes or the rejuvenation of established processes, mostly based on the application of heterogeneous catalysts as both reaction booster and energy trapper (Matros and Bunimovich, 1996). The complexity of RFO implies that the development of transient operation procedures is literally the key to success. Transient operation distinguishes RFO from steady state operation (SSO). Know-how is indispensable to introduce dedicated transients into reactor technology. It requires experimental work, modeling, and computer simulations.
The basic idea of RFO for manipulation of the surface coverage of a catalyst was discussed in Chapter 3. Further reactor development resulted in two novel concepts, so called RFO with temporarily lower feed concentration and RFO with reactor side feeding. These concepts have been presented in Chapters 4 and 5, respectively. In this Chapter 6, general conclusions and recommendations are discussed.

GENERAL CONCLUSIONS

The research work presented in this thesis focuses primarily on the development of a transient reactor operation procedure for manipulation of catalyst surface coverage as induced by periodic flow reversals. It was argued that traditional RFO with its long period of switching time is not suitable to maintain a dynamic state of the catalyst surface. Switching the flow direction should be carried at intervals in the order of seconds, which is a factor 1000 shorter than in traditional RFO. The selective oxidation of NH$_3$ was arbitrarily chosen as a model reaction as it produces various products. Therefore, this reaction provides both conversion and selectivity issues, which were studied in order to explore the potential benefits of RFO. The research work consisted of modeling and simulation, design of a reactor and an experimental set-up, and experimental work. Steady state experiments were performed to validate a kinetic model from the literature with respect to a different catalyst, reactor, and residence. The experimental results of the SSO were then used as base case to judge the potential of RFO. For RFO, the switching time was identified as the most important variable, and its effect on conversion and selectivity was studied. Other process variables like temperature, ammonia-to-oxygen feed ratio, and gas residence time, were investigated as well.

Three regimes of operation were considered during RFO. When the switching time is larger than the gas residence time, the regime is categorized as in a quasi-steady state. When the switching time is shorter than the gas residence time, the regime is called sliding or in relaxed steady state. The regime is dynamic when the switching time is comparable with the gas residence time. The research work involved three modes of reactor operation: regular RFO, RFO with temporarily lower feed concentration, and RFO with reactor side feeding. All reverse flow experiments were necessarily carried out in the quasi-steady state regime due to limitations of the switching valves when switching times were shorter than 2 s.

Regular reverse flow operation

Regular RFO always induces a lower NH$_3$ conversion than SSO does, regardless the switching time. A more profound decrease occurs in particular
when the switching time is much smaller than the gas residence time. Under such conditions, a dead gas volume is present in the central part of the reactor, which adds extra to low level of the \( \text{NH}_3 \) conversion because only part of the catalyst in the reactor is actively used.

If the switching time is much larger than the gas residence time, the \( \text{NH}_3 \) conversion in regular RFO approaches the value for SSO, but definitely never exceeds it. Selectivity changes due to flow reversals are minor when compared to SSO. At fixed switching time, an increase of the gas residence time during RFO causes a lower \( \text{NH}_3 \) conversion and a lower selectivity to \( \text{N}_2\text{O} \) at lower levels than in SSO. The opposite holds for the selectivities to \( \text{N}_2 \) and \( \text{NO} \).

When increasing the temperature, the conversion of \( \text{NH}_3 \) in RFO becomes considerably lower than in SSO. The selectivity to \( \text{N}_2 \) is higher at low temperature, while the selectivities to \( \text{NO} \) and \( \text{N}_2\text{O} \) are lower. At high temperature, the selectivities of RFO and SSO are almost the same.

Increasing the concentration of oxygen in the feed does not improve the conversion of \( \text{NH}_3 \) in RFO. Therefore, the differences in conversion between RFO and SSO are somewhat larger at higher oxygen concentration. Simultaneously the selectivity to \( \text{N}_2 \) decreases during RFO, although it is still higher than during SSO. The selectivity to \( \text{NO} \) in RFO is always lower than in SSO. At high oxygen concentration, even less \( \text{NO} \) is produced, while the selectivity to \( \text{N}_2\text{O} \) largely improves up to a higher level than in SSO.

Asymmetric operation of the reverse flow reactor causes a larger decrease of the \( \text{NH}_3 \) conversion compared to symmetric operation, while selectivity changes are minor.

Reverse flow operation with temporarily lower feed concentration

Reverse flow operation with temporarily lower feed concentration was developed with the aim to improve reactor conversion and selectivity, notably the conversion losses met during regular RFO. The crucial parameter in this case is the time period of lower feed concentration \( (t_L) \), while the switching time is still of interest. The conversion of \( \text{NH}_3 \) in RFO with concentration programming indeed can be improved at 573 K, which results in better values than for regular RFO, even exceeding conversion in SSO. Over a wide range of \( t_L \), the selectivity to \( \text{NO} \) is considerably improved, and values even higher than in SSO were reached. Accordingly, the selectivities to \( \text{N}_2 \) and \( \text{N}_2\text{O} \) were lower than in SSO. A major drawback of RFO with temporarily lower feed concentration is a decrease of all production rates.

At higher oxygen content of the feed, the \( \text{NH}_3 \) conversion in RFO with temporarily lower feed concentration is about 3% lower than in SSO. The
selectivity to \( \text{N}_2 \) is always an absolute 20 to 30\% lower compared to SSO, while it is 20 to 40\% larger for \( \text{NO} \), with a maximum around 2 vol.\% \( \text{O}_2 \) in the feed. For \( \text{N}_2\text{O} \), the selectivity is 10 to 20\% below the SSO levels, but slightly above it if the oxygen content of the feed increases up to 3 vol.\%.

An increase of the temperature to 673 K induces smaller differences of the \( \text{NH}_3 \) conversion between RFO and SSO. In the range 573-673 K, the selectivity to \( \text{NO} \) improves due to higher temperature with about 50\%, while values for \( \text{N}_2 \) and \( \text{N}_2\text{O} \) decrease with 30 and 15\%, respectively. Feed concentration programming with a larger \( \text{NH}_3 \) amplitude invokes a little lower ammonia conversion. The selectivity to \( \text{N}_2 \) now increases, as does the selectivity to \( \text{N}_2\text{O} \) at the expense of \( \text{NO} \).

**Reverse flow operation with reactor side feeding**

Reverse flow operation with reactor side feeding was subsequently proposed to reach similar improvements as met in RFO with temporarily lower feed concentration, but without the clear decrease of the production rates.

The feed positions appear a crucial parameter next to the switching time. This mode of operation distinguishes different zones in the reactor. In between the two feed positions, a reverse flow region exists. At each end of the reactor, there is an interrupted flow region where the flow is either in one direction only or it is interrupted. In the latter situation, this region acts as a batch reactor.

When the switching time is shorter than the gas residence time in once-through operation, simulations showed that shifting the feed positions to the reactor center results in better conversion of \( \text{NH}_3 \). The selectivity to \( \text{NO} \) would increase from 77 to 90\% at the expense of \( \text{N}_2\text{O} \) and notably \( \text{N}_2 \). When the switching time is larger than the gas residence time in once-through operation, only minor changes of conversion and selectivities are predicted from simulations.

The experiments, although they all were performed in the quasi-steady state regime, confirm the trend of more conversion, more \( \text{NO} \) and less \( \text{N}_2\text{O} \), if a shorter switching time is applied. It is noteworthy that effects of RFO were already observed in the quasi-steady state regime. Effects of temperature, residence time, and feed position were studied.

It appears that short switching times should be applied in order to take full advantage from the contribution of the interrupted flow regions to conversion and selectivities. At large switching time, ammonia in the interrupted flow region is completely converted shortly after the flow has been stopped, which has a negative influence on the overall performance.
Kinetic modeling and reactor modeling

A kinetic model from the literature, developed for ammonia oxidation over Pt/Al₂O₃ on the basis of elementary reaction steps, was validated for the catalyst used in this work. This model with minor adaptations appeared sufficiently adequate to describe conversion and selectivities of the currently performed steady state experiments. This allowed the application of the kinetics for prediction of reverse flow experiments.

A reverse flow reactor model was formulated for regular RFO, RFO with temporarily lower feed concentration, and RFO with side feeding. The model appeared capable to describe most trends, which were observed from reverse flow experiments. Moreover, the model was applied to predict the events on the catalyst surface as a result of reverse flow operation. It was clearly demonstrated that RFO affects the coverage of the catalyst with adsorbed species. Both higher and lower coverage of notably oxygen could be achieved, although the complexity of the process not always allowed to relate such behaviour to the overall performance of the process. For RFO with side feeding, model predictions showed that short switching times add to the conversion because of on-going NH₃ oxidation in the interrupted flow region, while there is a depletion of N-containing species at larger switching times.

RECOMMENDATIONS

The novel concepts of RFO with temporarily lower feed concentration and RFO with reactor side feeding have shown that manipulation of the catalyst surface coverage provides options to increase the conversion of NH₃ and to direct the selectivity toward a specific product. Nevertheless, some drawbacks of these operation modes became apparent. Experimental limitations concerning the application of short switching times hindered to fully explore the RFO potential under such conditions, which seems more promising as predicted from computer simulations. Moreover, many of the observed phenomena are not yet fully understood due to the complexity of the reverse flow process when the catalyst surface is in a dynamic state. It is clear that more research is required.

Kinetic modeling and reactor modeling

The development of transient kinetic models is indispensable for RFO, aiming at manipulation of the catalyst surface coverage. Maintaining the catalyst in a dynamic state requires rather fast switches of the flow direction, meaning that accumulation effects in mass balances for the catalyst surface should be taken into account. Although the current kinetic model is capable to describe trends,
observed during experiments, serious deviations between experiments and model predictions were sometimes apparent. It leaves ample opportunities to improve on the accuracy of the kinetics. This holds in particular for secondary reactions, which become more important when high conversion and selectivity to one specific product are aimed at.

Further modeling and simulation of RFO are required to define more precisely the conditions for improved conversion and selectivity. Therefore, future work should simultaneously involve heat balances into the reactor model, as practical applications will operate under adiabatic conditions with exploitation of autothermal behaviour. Moreover, heat balances should be considered from a viewpoint of safe reactor operation, which points to avoiding run-away and to dedicated start-up and shut-down procedures. Bifurcation analysis is a point of interest in this respect to study reactor stability for the development of a control strategy.

**Reactor design and operation**

Computer simulations, presented in Chapter 5 of this thesis, indicate that more benefits can be expected from reverse flow operation with side feeding if switching times smaller than the residence time can be applied. This item was not validated with experiments due to the limitations of the set-up. It requires attention for the development of fast switching valves, which can be positioned near to the catalyst bed in order to avoid as much as possible dead volumes in the inlet and outlet lines. In particular for large scale operation as necessary for bulk processes, such a development is a real challenge, which could benefit from a technology push, once this mode of operation seems economically feasible. Figure 6-1 shows an option for a fast switching valve that could be worthwhile for further investigation. The principle is a rotating switch valve at either end of the reactor.

![Diagram](image_url)
A = pre-exponential factor (s⁻¹ or s⁻¹ atm⁻¹)
C = concentration (mol m⁻³)
D_{ef} = axial dispersion coefficient (m² s⁻¹)
E_a = activation energy (J mol⁻¹)
E(t) = residence time distribution function (s⁻¹)
F = volumetric flowrate (m³ gas s⁻¹)
f = time fraction for high concentration
FR = concentration feed ratio of NH₃ to O₂ (-)
G_{of} = Gibbs energy of formation (kJ mol⁻¹)
k = reaction rate coefficient (s⁻¹ or s⁻¹ atm⁻¹)
L = reactor length (m)
L_a = feed position (m)
L_{min} = distance between two feed positions, L_r - 2L_a (m)
L_r = total reactor length (m)
N = response of the turn-over frequency (s⁻¹)
n = numbers of cycles, number of masses analyzed (-)
p_i = partial pressure of gas component i (atm)
R = ideal gas constant (m³ atm mol⁻¹ K⁻¹), or reactor
r = dimensionless radial position (-)
\tau_k = reaction rate of step k (mol component mol sites⁻¹ s⁻¹)
T = temperature (K)
t = time (s)
t_c = cycle time (s)
t_s = switching time (s)
u = absolute value of superficial velocity (m s⁻¹)
u_s = superficial velocity (m s⁻¹)
V_r = reactor volume (m³ reactor)
z = dimensionless axial position (-)
z_a = dimensionless feed axial position (-)
{ } = top site (-)
( ) = hollow site (-)

Greek letters

\alpha = ratio of switching time to gas residence time (-)
\varepsilon_b = bed porosity (m³ gas m⁻³ reactor)
\rho_b = bed density (kg cat m⁻³ reactor)
\delta = \text{int}[L_a/(L_r - 2L_a)], numbers of gas flow interrupted (-)
\Delta = conversion or selectivity difference between RFO and SSO
\theta_j = surface coverage of component j
\tau_o = gas residence time in once-through operation (s)
\( \tau_{tavg} = \) time-average gas residence time (s)  
\( \Phi = \) catalyst mol site (moles of catalyst sites kg\(^{-1}\text{cat}) \)  
\( \kappa = +1 \) when the flow direction to right and -1 when the flow direction to left  
\( \phi = \) lateral interaction energy (kJ mol\(^{-1}\))  
\( \Delta = \) difference (-)

**Superscripts**

\( hs = \) hollow site  
\( 0 = \) feed  
\( ss = \) steady state  
\( ts = \) top site

**Subscripts**

\( A = \) component A  
\( b = \) bed  
\( c = \) cycle  
\( dyn = \) dynamic  
\( H = \) time period at high concentration  
\( i = \) component in the gas phase  
\( in = \) inlet  
\( j = \) component in the solid phase  
\( k = \) elementary step, \( k = 1, 2, 3, \ldots, 13 \)  
\( L = \) time period at low concentration  
\( \text{max} = \) maximum  
\( \text{min} = \) minimum  
\( o = \) steady state operation, vacant sites (top, hollow)  
\( qss = \) quasi-steady state  
\( r = \) reactor  
\( s = \) switching, superficial velocity  
\( sli = \) sliding  
\( ss = \) steady state  
\( tavg = \) time-average  
\( \rightarrow = \) flow direction to right  
\( \leftarrow = \) flow direction to left
A

B
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C

D
E

F

G

H

I

J

K

M

N

O

P

R

S


Website1: http://www.uhde.biz/kompetenzen/technologien/duengemittel_tech_uebersicht_cen.html


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Eindhoven, July 2005

Yogi W. Budhi
List of Publications

Journals


Presentations


Other selected paper

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After finishing his Bachelor of Engineering from the Chemical Engineering Department at ITB in 1995, he was first appointed in PT Pupuk Kalimantan Timur, a fertilizer plant. However, he returned to ITB. His research at ITB concerned process development topics like integration of a reformer and heat exchanger, biomass gasification, and spray drying, which resulted in more than 25 professional publications. In addition, he invented a novel technique of palm sugar production, which was filed for a patent application. He also followed various training courses, both in teaching and catalysis and reaction engineering.

Professionally, he is a member of the Chemical Engineers Chapter of the Institute of Engineers, Indonesia (BKK-PII), and of the Indonesian Catalysis Society (MKI). He was one of the founders of the Indonesian Process Technology Forum (Fortep) and secretary of the superintendent board of the Center for Assessment of Industry, Technology, and Business (PPITB). Currently, he develops a private research group concerning transient reactor operation, called Wibisono-tech.

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Reverse flow operation (RFO) is a novel engineering tool for control of catalyst surface coverage, which allows to manipulate the selectivity. It was argued that traditional RFO with its long period of switching time is not suitable to maintain a dynamic state of the catalyst surface. Switching the flow direction should be carried out at intervals in the order of seconds, which is a factor 1000 shorter than in traditional RFO. However, regular RFO always induces a lower conversion than steady state operation (SSO) does, regardless the switching time. Novel concepts of RFO are proposed: (1) RFO with temporarily lower feed concentration, (2) RFO with reactor side feeding. This thesis addresses a theoretical study and experimental work of RFO for selective oxidation of NH₃ over alumina-supported platinum catalyst. Focus was on the development of a transient operation procedure of a fixed bed reactor, which is the vital engineering tool to perturb the surface coverage of a catalyst. The primary goal is to demonstrate that RFO may create dynamic changes of active site coverages, which may change the conversion and selectivity when compared to SSO.