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# Maleic anhydride yield during cyclic n-butane/oxygen operation

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# ABSTRACT

Cycling catalyst between a net oxidizing and reducing gaseous environment has been practiced commercially to produce maleic anhydride from n-butane over vanadium pyrophosphate. Typically, the oxidation period is less than 1 min to minimize catalyst inventory. In this study, the effect of the oxidation period on maleic anhydride productivity was assessed in the range of 0.3–10 min. Irrespective of the feed gas composition during the reduction period, the productivity increased linearly with the oxidation soak time in air. A full range of reducing conditions was examined from the pure redox mode (10% n-butane in argon) to highly oxidizing conditions typical of fixed bed operation (1.4% n-butane and 18.1% oxygen). On average, maleic anhydride yield increased by up to 50% when the oxidation time was extended from 0.3 to 10 min. The maleic anhydride yield was lowest under redox mode and it was highest when the feed composition was close to equimolar in n-butane ( $\sim$ 6%) and oxygen. Our results show that industrial CFB reactor performance may be improved considerably by efficient regeneration of the catalyst and optimization of the reducing feed gas composition.

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# 1. Introduction

For almost three decades, maleic anhydride (MA) has been commercially produced by partial oxidation of n-butane over vanadium phosphorous oxide (VPO) catalysts in fixed beds, fluidized beds and other reactor types [1]. In one of the most recent developments, DuPont commercialized circulating fluidized bed (CFB) reactor technology in which the reduction and oxidation zones were conducted in separated vessels [2]. The reactor consisted of a high gas velocity riser coupled to a turbulent fluidized bed (fast bed), a counter current flow fluidized bed regenerator and a stripper (gas up-solids down). The gas in the fast bed riser contained a high concentration of n-butane that carried the catalyst upwards. The reduced catalyst was transferred to a stripping vessel in which the product gas was separated from the catalyst; the catalyst was then transferred to a fluidized bed regenerator where it was oxidized by air. The freshly oxidized catalyst was circulated back to the fast bed of the riser through a stand pipe and subsequently to the riser where n-butane reacted with catalyst oxygen to produce maleic anhydride, CO, CO<sub>2</sub> and water. This configuration was designed to achieve high maleic anhydride productivity and selectivity due to the utilization of selective catalyst surface lattice oxygen. One of the original concepts involved operating in the pure redox mode in which the reducing zone contained n-butane (+recycle gas) and air was fed to the regenerator. However, to maximize reaction rates and, thereby, minimize catalyst inventory, molecular oxygen was introduced into the reducing zone. Minimizing non-selective gas phase combustion of n-butane by the molecular oxygen was achieved by carefully distributing the oxygen across the fast bed at three levels.

Maintaining the VPO surface highly oxidized is a major challenge for fluidized bed processes that operate with high n-butane concentrations. In CFB reactors, there is an economic trade-off between solids residence time in the regenerator, solids circulation rate and selectivity/conversion: increasing catalyst inventory in the regenerator will increase n-butane conversion and maleic anhydride selectivity in the fast bed/riser but catalyst inventory increases total investment costs. Moreover, yield is sensitive to flow patterns in each of the vessels: gas and solids bypassing and solids gulfstreaming must be minimized to ensure an efficient contact between the two phases. Mal-distribution or short circuiting of the solids in the regenerator results in an overly reduced catalyst and potentially lower maleic anhydride yields. Understanding and accounting for the solids residence time distribution in the vessels becomes critically important in the design stage when translating laboratory scale and pilot scale experimental data to the commercial scale.

There has been some controversy on the role of lattice oxygen versus surface oxygen on maleic anhydride selectivity and n-butane conversion. There is a general agreement in the literature that the surface lattice oxygen is more selective to n-butane conversion to maleic anhydride [3–7]. However, the exact role of this oxygen species or other species – adsorbed and molecular oxygen – during the reaction has not been fully identified. The "loosely bound" surface oxygen and chemisorbed (adsorbed) oxygen on



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the surface of the catalyst were believed to be the main source of non-selective conversion of n-butane [8]. Creaser et al. [9] also showed that surface oxygen was less selective compared to lattice oxygen in the oxy-dehydrogenation of propane. Early in the development stages of DuPont's n-butane partial oxidation program, we installed a regenerator stripper in the pilot plant to eliminate "loosely bound" surface lattice oxygen to achieve higher maleic anhydride selectivity. This vessel was removed in the commercial design, since its efficacy remained unproven during the trials.

Wang et al. [10] conducted forced concentration cycling tests in a microbalance reactor and proposed that both lattice oxygen and adsorbed oxygen were selective to maleic anhydride. However, the contribution of the lattice oxygen was lower than the adsorbed oxygen species. Gascón et al. [11] and Centi et al. [12] also confirmed the active role of adsorbed surface oxygen on conversion of n-butane. Under fuel rich conditions, Gascón et al. [11] observed a decrease in n-butane conversion during reduction by increasing purge time between oxidation and reduction periods due to elimination of physically adsorbed surface oxygen. These findings suggest that contrary to the common belief on the selective role of lattice oxygen in the reaction, the participation of lattice oxygen is not enough to maintain a high rate of reaction and therefore the presence of gas phase oxygen is essential to supply oxygen to the reaction through adsorption on the surface. A general conclusion of these findings may suggest that the VPO catalyst is not naturally suitable for redox reactions under high n-butane to oxygen ratio. To prevent the side reactions under fuel rich conditions (higher selectivity) and to maintain a higher reaction rate, Ballarini et al. [1] suggested that the presence of co-feed oxygen during the reaction is always required to prevent excessive reduction of V<sup>5+</sup> and  $V^{4+}$  as the catalyst active sites.

Many researchers have reported maleic anhydride yield improvement as a result of increasing VPO catalyst regeneration time. Emig et al. [13] showed that under cyclic redox operating conditions, maleic anhydride production rates increased by a factor of three when the catalyst regeneration time was increased from 30 min to 18 h. During their forced concentration cycling experiments, Patience et al. [4] observed a higher level of nbutane conversion and maleic anhydride selectivity during the first few minutes after switching the feed from oxidizing to reducing conditions; they attributed the high initial reaction yields to the accumulation of selective oxygen species (most likely surface lattice oxygen) during a 40 min oxidation period. Lorences et al. [14] also showed that exposure of the catalyst to an oxidizing environment for 48 h provided twice as much surface oxygen compared to a 1 h oxygen treatment. They showed that soaking the catalyst with oxygen could increase the maleic anhydride yield by up to four times the steady state value. Contrary to these findings Huang et al. [15] reported that the catalyst may become inactive due to over oxidation for a long time. Catalyst deactivation could be probably due to accumulation of highly oxidized vanadium sites (V<sup>5+</sup>) or sintering of the catalyst surface during relatively long oxidation periods. When the catalyst is exposed to air with even low amounts of water vapour (<3%), the oxidation state can rise above 4.5 and thereby deactivate the catalyst [16]. Irreversible oxidation was only possible when water vapour was co-fed. In general, as long as the water vapour partial pressure is low, longer regeneration times enhance catalyst performance.

In experimental facilities, oxidation times of up to 10 min are commonly tested. However, in commercial operation, the mean residence time of the solids in the regenerator may be as low as 1 min [17]. The economic incentive for low residence times translates to lower catalyst inventory and thus lower operating costs but the penalty in reduced maleic anhydride yield must also be considered. In this study, we have systematically varied catalyst oxidation time, reduction feed composition and temperature to assess their

# Table 1

Technical specifications of DuPont's calcined VPO catalyst.

Composition	Color	$ ho_{\rm p,}~{\rm kg}/{\rm m}^3$	BET, m <sup>2</sup> /g	$d_p, \mu m$
(VO) <sub>2</sub> P <sub>2</sub> O <sub>7</sub> + 10% SiO <sub>2</sub>	Gray/green	1700	34.9	70

impact on maleic anhydride production rates. The catalyst oxidation times corresponded to the values tested in DuPont's laboratory scale equipment, pilot plant and commercial reactor. Several feed compositions were tested that represented typical operating conditions of fixed bed and fluidized bed reactors as well as the CFB technology. The experimental methodology proposed in this study should be helpful in assessing emerging CFB technologies including: Chemical Looping Combustion (CLC) [18], Chemical Looping Reforming (CLR) for hydrogen and CO production [19], propane oxidation to acrylic acid [20], propane oxy-dehydrogenation [9], hot gas desulphurization (ZnS–ZnO) [21], methanol to olefins (MTO) [22] and methanol to gasoline (MTG) [23].

# 2. Experimental

#### 2.1. VPO catalyst preparation

The transient redox experiments were conducted on DuPont catalyst that was calcined in the industrial CFB reactor [16]. The precursor was synthesized in an organic solvent, dried and then micronized to less than 2  $\mu$ m. The micronized powder was slurried with polysilicic acid and spray dried. The average particle diameter was approximately 70  $\mu$ m with 10% silica and the BET surface area of the calcined catalyst was about 35 m<sup>2</sup>/g – Table 1. The predominate phase was vanadium pyrophosphate – (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (VPP).

The catalyst powder was sieved to a particle size between 125 and 180  $\mu$ m prior to experimentation. This range of particle size is commonly used in the literature [11]. Due to the high porosity and relatively low reaction rates, the intra-particle mass transfer resistance was neglected. Approximately 500 mg of calcined catalyst was used for all transient redox experiments. Before beginning an experiment, the fresh catalyst was activated by a mixture of 1.4% n-butane in 18.1% oxygen (balance argon) for 24 h. The base case temperature was 380 °C and the total feed flow rate was 40 mL/min (STP). Catalyst activity was reasonably stable after this time period.

#### 2.2. Experimental setup

The transient redox experiments were conducted in a 7 mm ID quartz tube micro-reactor that was placed in an electrical furnace. The process flow diagram of the micro-reactor experimental setup is shown in Fig. 1. Four mass flow controllers (MFC) maintained the feed flow rates to the reactor. The first three MFCs (A-C) were used to mix the feed streams for the reaction and also to feed oxygen during catalyst oxidation. The feed streams were taken from three gas bottles: 10 vol% n-butane in argon, 21 vol% oxygen in argon and 99.9 vol% argon. The fourth mass flow controller (D) was used to purge the reactor with argon between the reduction and oxidation half-cycles and also between two redox cycles. An electrically controlled 6-way valve was used to switch between the feed streams at a specified time sequence. There was also a possibility for manual flow rate measurements by directing different gases to a bubble flow meter using proper valve positions. The CATLAB software developed for the micro-reactor system (from Hiden Analytical) controlled the operation of the MFCs and the reactor furnace as well as the automated switching valve. Downstream of the reactor, a small fraction of the exit stream ( $\sim 1\%$ ) was sent to an online mass spectrometer (Quadrupole type QIC-20 from Hiden Analytical) for real time measurement of gaseous products (CO, CO<sub>2</sub> and water) as well as un-reacted n-butane and oxygen. The frequency



Fig. 1. Micro-reactor experimental setup.

of the measurements in the mass spectrometer was in the order of 2–5 data point per second. The main part of the effluent stream was sent to an aqueous quench to absorb product acids, in which the electrical conductivity was monitored in real time to estimate the evolution of the product acids. To cross check the validity of the conductivity measurements and also to identify the acid product distribution, a liquid sample from quench was taken at the end of each redox cycle and analyzed by HPLC (Modular ProStar unit from Varian).

# 2.3. Redox experiments

To study the effect of catalyst oxidation time and reduction feed composition on reactor performance, experiments at four oxidation times and six feed compositions were conducted. A list of experimental conditions is presented in Table 2. The reduction feed compositions were selected to cover the full range of industrial operation: from fuel rich conditions typical of CFB reactors, with as much as 10% n-butane, to fuel lean conditions, characteristic of fixed bed reactors with as little as 1.4% n-butane in the feed. The lower bound concentration of n-butane in the feed to the reactor was selected such that to avoid the explosion limits (1.8% n-butane in air). The catalyst oxidation times were varied from 10 min (standard for bench top laboratory experiments) to as low as 0.3 min that represents conditions in an industrial CFB reactor. Finally, to observe the effect of temperature on the reaction yield, two selected feed compositions were run at 360 and 400 °C with a 10 min reoxidation period. The selected runs corresponded to the actual industrial fuel rich conditions (i.e.  $O_2/n$ -butane = 0.3 and 1.2).

The micro-reactor setup was designed so that the operation of a circulating fluidized bed reactor could be simulated by switching between reduction and oxidation feed streams over the fixed catalyst bed. In this way, data interpretation was simplified in that the gas phase hydrodynamics were much less complicated com-



**Fig. 2.** Effect of oxidation time on maleic anhydride production rate (feed flow rate: 40 mL/min (STP), temperature: 380 °C).

pared to fluidized bed reactors. For each redox condition described in Table 2, a series of at least 5 identical redox cycles were conducted. The catalyst activity was then calculated by averaging the results obtained for each repeated run. Adequately long purging between the redox half-cycles and between repeated full cycles ensured the removal of gas phase oxygen and reaction products from the reactor and the connecting lines and provided identical conditions for each redox cycle.

For each redox experiment, a time sequence of events was programmed in the CATLAB software including: flow rate of each MFC, valve switch moments, and temperature. The catalyst was first heated under an inert argon stream until the desired temperature was achieved and then exposed to a series of 5–8 cycles. Each oxidation half-cycle was followed by a 10 min purge. The reduction half-cycle lasted for 2 min while there was 30 min of purging between redox cycles.

# 3. Results and discussion

#### 3.1. Effect of redox parameters

#### 3.1.1. Oxidation time

The oxidation step has a significant effect on maleic anhydride yield, even under fuel lean conditions. Based on the extensive literature data, we expected that the oxidation time would improve maleic anhydride yield for fuel rich conditions but there would be little to no effect for fuel lean conditions. Fig. 2 shows that the average maleic anhydride production rates increase linearly with an increase in the catalyst oxidation time irrespective of the reduction feed composition ( $O_2$ /n-butane ratio). In most of the experiments, where there was some oxygen co-fed with n-butane, the maleic anhydride yield improved by up to 50% by increasing the catalyst oxidation time from 0.3 to 10 min. The increase in maleic anhydride production was much more noticeable in the pure redox mode

Table	2
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Experimental conditions of transient redox runs<sup>a</sup>.

Reduction compositio	n, vol%	O <sub>2</sub> /n-butane ratio	Oxidation time, min	Temperature, °C
n-butane	Oxygen			
9.9	0.0	0.0	0.3-10	380
8.8	2.5	0.3	0.3-10	360, 380, 400
7.7	4.8	0.6	0.3-10	380
6.4	7.5	1.2	0.3-10	360, 380, 400
3.6	13.4	3.7	0.3-10	380
1.4	18.2	13.6	0.3-10	380

<sup>a</sup> Reduction time: 2.0 min; average feed flow rate: 40 mL/min (STP).



**Fig. 3.** Effect of feed composition on maleic anhydride production rate (feed flow rate: 40 mL/min (STP), temperature: 380 °C).

 $(O_2/n$ -butane = 0.0). In this case, the maleic anhydride production increased by a factor of 3.5 times after extending the catalyst oxidation time from 0.3 to 10 min. These results are similar to the findings of Emig et al. [13] where they reported an increase in the maleic anhydride production rate by a factor of three when the catalyst regeneration time was increased from 30 min to 18 h. The time allowed for catalyst oxidation in the lab scale micro-reactor could be actually correlated to the solids residence time in the regeneration section of an industrial CFB reactor. These results show how important it could be to optimize the solids residence time in the regenerator and the ability to supply oxygen. The higher observed rates are believed to be due to the higher availability of the selective surface lattice oxygen.

# 3.1.2. Feed composition

Fig. 2 shows the relationship between oxidation time and maleic anhydride production rate. The same data is re-plotted in Fig. 3 to demonstrate the effect of feed composition on productivity: maleic anhydride production rate increases with increasing n-butane concentration up to a 1:1 feed composition. The maximum maleic anhydride production rate exceeds 160 gMA/h/kg VPO when the feed concentrations of n-butane and oxygen are equimolar. MA production drops by about 15% at conditions typical of turbulent fluidized beds and then by another 30% in fuel lean conditions characteristic of fixed bed operation. The lowest production rates are under purely redox conditions. Clearly, maintaining sufficient oxygen together with n-butane is critical to maintaining high maleic anhydride productivity. This observation could be attributed to the opposing positive and negative effects of elevated n-butane concentration in the feed to the reactor. The positive effect is related to the increased reaction rate with high n-butane concentrations. However, high n-butane concentrations negatively affect the catalyst performance by decreasing the catalyst oxidation state and by accelerating catalyst deactivation (loss of surface oxygen) or probably due to higher rate of surface carbon formation.

# 3.1.3. Temperature

We studied the effect of temperature on maleic anhydride production rate at two feed compositions:  $O_2/n$ -butane = 0.3 and 1.2. The latter condition represents typical feed composition of a CFB plant while the former corresponds to the exit conditions when the plant is run at high inlet n-butane concentrations. The latter ratio is close to the optimum feed ratio that resulted in the highest maleic anhydride productivity. As is shown in Fig. 4, temperature has little effect on productivity when the n-butane feed rate is high compared to the oxygen feed rate even though the catalyst was soaked



Fig. 4. Effect of temperature on maleic anhydride production rate (oxidation time: 10 min, feed flow rate: 40 mL/min (STP)).

in air for 10 min. On the other hand, temperature has a measurable effect on yield with a close to an equimolar feed composition of oxygen and n-butane: the productivity increased approximately 10% when the temperature was increased by 20 from 380 °C and it dropped by 40%, when the temperature was decreased by 20 °C. This data is consistent with previous studies that showed increasing the temperature during re-oxidation enhanced the oxidation rate of the VPO catalyst during reduction [11,15]. More oxygen is incorporated into the surface lattice resulting in increased maleic anhydride productivity.

### 3.2. Transient maleic anhydride rates

We measured the transient maleic anhydride production rates by monitoring the electrical conductivity of the acid solution accumulated in the liquid quench that was located downstream of the micro-reactor (Fig. 1). The results were in agreement with our observations: the transient production rates increased with increasing the oxidation time. The transient rates presented in Fig. 5 show that the initial rates of maleic anhydride (at initial moments of the curves) increase by increasing the oxidation time before each reduction cycle. This could be due to the higher accumulation of selective oxygen species on the catalyst surface when the catalyst is exposed to the oxidation environment for a longer period of time. Similar high initial catalyst activities were reported by Patience et al. [4] and Lorences et al. [14], at the first few minutes of reduction period after an extensive catalyst oxidation.



**Fig. 5.** Maleic anhydride transient production rates (feed flow rate: 40 mL/min (STP), temperature: 380 °C, O<sub>2</sub>/n-butane: 0.0).



Fig. 6. VPO catalyst deactivation during redox operations at fuel rich conditions (feed flow rate: 40 mL/min (STP), temperature:  $380 \degree C$ , oxidation time:  $10 \min, O_2/n$ -butane: 0.0).

### 3.2.1. Catalyst deactivation

During the transient redox experiments, we observed that at relatively high n-butane concentrations in the feed ( $O_2/n$ -butane  $\leq 0.3$ ), the catalyst undergoes a considerable deactivation during the reduction period even with a relatively long oxygen pre-treatment before each reduction cycle (10 min). The catalyst deactivation was characterized by a stepwise decrease in the maleic anhydride transient rates during 5–8 consecutive redox cycles under the same operating conditions. Fig. 6 demonstrates the transient maleic anhydride rates selected from eight consecutive redox cycles at the conditions where there was no oxygen in the reduction feed. A significant decrease in the maleic anhydride transient rate could be observed by exposing the catalyst to these consecutive redox cycles. These data show that the deactivation of catalyst could not be compensated even by 10 min of catalyst oxidation before each reduction cycle.

When the catalyst oxidation time is relatively short, even in the presence of some oxygen in the reduction feed ( $O_2$ /n-butane  $\leq 0.6$ ), the catalyst still suffers a slight deactivation during consecutive redox cycles. Generally, this effect is more noticeable when the oxygen to n-butane molar ratio in the feed falls below 0.3. Under these conditions, the catalyst deactivation occurs irrespective of the duration of oxidation period prior to each reduction cycle (Fig. 6). These results suggest that to maintain a relatively high production rate at fuel rich conditions, the feed to the reactor must have an appreciable amount of oxygen to prevent catalyst over reduction. Also, even in the presence of oxygen in the reduction feed, efficient catalyst oxidation would still be required to compensate for the catalyst deactivation during reduction under fuel rich conditions.

# 4. Conclusions

Maleic anhydride production rate is sensitive to catalyst oxidation time and reduction feed composition. Irrespective of the reduction feed composition, the average maleic anhydride production rate in a redox cycle could be increased by up to almost 50% by extending the catalyst oxidation time from 0.3 to 10 min. Maleic anhydride production rates increase even with a feed composition containing 1.4 vol% n-butane in air. The effect of catalyst oxidation on maleic anhydride production becomes more important when operating under fuel rich conditions. Under such conditions, an improvement of the order of 3.5 times in maleic anhydride production rate could be expected by extending the catalyst oxidation time to 10 min. A near equimolar feed of 6% n-butane and oxygen resulted in the highest maleic anhydride production rate. The transient maleic anhydride rate data showed that to prevent the catalyst deactivation and to maintain a high production rate at fuel rich conditions, the feed to the reactor must have an appreciable amount of oxygen. These data also suggested that efficient catalyst deactivation even at the presence of relatively large amounts of oxygen in the reduction feed.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2010.03.011.

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