



## Chromium catalyzed tetramerization of ethylene in a continuous tube reactor—Proof of concept and kinetic aspects

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### ABSTRACT

Highly selective processes for the tri- and tetramerization of ethylene offer an interesting alternative to conventional ethylene oligomerization processes that are constrained by yielding mathematical distributions of linear  $\alpha$ -olefins. This inherent lack of selectivity often makes it difficult for full slate producers to respond to changing market demands in each product segment. This is the first known report on the continuous tri- and tetramerization of ethylene in a continuous plug flow tubular reactor. Standard run times of 10 h and a catalyst comprising  $\text{Cr}(\text{acac})_3$ , 1,2-dimethylpropyl-bis(diphenylphosphino)amine ligand and the aluminum-based activator MMAO-3A was used. Activities exceeding 3,700,000 g/(g<sub>Cr</sub> h) and combined selectivities for 1-hexene and 1-octene of more than 90% were achieved. The influence of temperature, catalyst concentration, and ethylene concentration in the reactor on reaction rate (catalyst activity) and selectivity has also been investigated. In addition, supporting kinetic studies were performed in a semi-batch reactor setup with the aim to explain the influence of ethylene concentration on product selectivity found in the continuous runs. It was found that the reaction orders in ethylene for 1-hexene and 1-octene are different, with 1-octene formation being significantly more sensitive to ethylene concentration.

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## 1. Introduction

Linear  $\alpha$ -olefins (LAOs) are versatile intermediates for the production of co-polymers (1-C<sub>4</sub> to 1-C<sub>8</sub>), plasticizer alcohols (1-C<sub>6</sub> and 1-C<sub>8</sub>), detergents (1-C<sub>12</sub> to 1-C<sub>14</sub>) and synthetic lubricants (1-C<sub>10</sub>, 1-C<sub>16+</sub>). Obviously, each of these compounds has its own market segment with distinctively different market size, growth, geographic demand and quality requirements. At present, the market for 1-olefins in the co-monomer range (specifically 1-hexene and 1-octene) is growing at an over-proportional 5.4–7.9% per annum while other segments are stagnating or even shrinking [1].

The development of new catalyst systems for the selective production of co-monomer grade 1-hexene and 1-octene is therefore highly desirable from an industrial point of view, due to the fact that conventional ethylene oligomerization processes based on the Cossee-Arlman mechanism [2] lead to mathematical product distributions (e.g., Schulz-Flory [3,4]) of  $\alpha$ -olefins. Although the selective trimerization of ethylene was discovered as early as the

late 1960's by Manyik et al. at Union Carbide Corporation [5], it was Reagan at Chevron Phillips Chemicals [6,7] who picked up the discovery in the late 1980's and developed an industrially viable technology that was later commercialized in Qatar in 2003 (47,000 ton/annum capacity).

In the ensuing years a number of new trimerization catalysts were developed based on a variety of metals (including Cr, Ti and Ta), with the chromium-based systems showing the best long-term stability and highest efficiency [8]. Amongst others, diphosphine ligands with nitrogen ( $-\text{N}(\text{CH}_3)-$ ) [9] and bis-ethyl-amine ( $-\text{CH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2-$ ) bridges [10] as well as bis-(sulfanyl-ethyl)-amine ( $\text{RSCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{SR}$ ) ligands [11] were found to be effective ligands in combination with chromium. With only minor changes to the structure of some of these ligands a shift in reaction product selectivity away from 1-hexene in favor of 1-octene (via ethylene tetramerization) has been found [12–15]. Over the last few years a number of mechanistic [16–20] and theoretical (DFT)-studies [21] were carried out on chromium tri- and tetramerization systems, thereby providing some fundamental understanding on these novel reactions. Alternative triethylaluminum/aluminate-based activators have been described to find ways of activating the catalyst complex with other species than the expensive MAO [22]. Furthermore, recent kinetic investigations on

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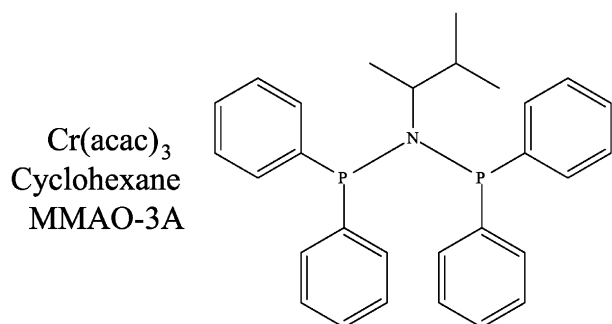


Fig. 1. Components of the ethylene tetramerization catalytic system used in this study.

the tetramerization of ethylene [23] have shown an ethylene concentration dependency on reaction rate in the order of 1.57 for the catalytic reaction in cumene. Despite these significant advances in catalyst design and fundamental understanding of chromium catalyzed ethylene tetramerization systems there are, to the best of our knowledge, no reported studies in the open literature on the application of this reaction in a continuous reactor configuration.

Herein we report the first study on Cr-catalyzed tetramerization of ethylene in a plug flow tubular reactor (PFTR). Consistent with some previous observations during semi-batch oligomerization reactions [23,24], a strong influence of ethylene concentration on C<sub>6</sub> vs. C<sub>8</sub> selectivity was found in these continuous runs. Therefore we carried out additional semi-batch experiments in order to determine the independent rate of formation for both 1-hexene and 1-octene, with respect to ethylene.

## 2. Experimental and methods

### 2.1. Catalytic system

All catalyst preparation steps were conducted under argon atmosphere and only purified and degassed cyclohexane was used as solvent (purification over alumina using a commercial SECA solvent purification unit). The catalyst system comprised Cr(acac)<sub>3</sub> as metal precursor, 1,2-dimethylpropyl-bis(diphenylphosphino)amine (DMP-PNP) as ligand and an isobutyl-modified methylaluminumoxane (MMAO-3A) as activator (Fig. 1). MMAO-3A and the chromium precursor were used as received from Akzo-Nobel and Strem, respectively. The ligand was synthesized according to standard literature procedures [25].

### 2.2. PFTR configuration

All continuous ethylene oligomerization experiments were carried out in a plug flow tubular reactor unit as depicted in Fig. 2. Both cyclohexane (A) and ethylene (B) were first fed in a controlled manner to a stirred tank (C) in which the ethylene dissolved in the solvent. The ethylene concentration in the solvent was always kept significantly lower than the maximum saturation concentration to avoid degassing of the solvent in the tubular reactor (D). Since less ethylene than theoretically possible dissolved into the liquid phase, the effective ethylene partial pressure in the liquid phase was usually significantly lower than the actual system pressure. Hereafter, the term  $P_{\text{effective}}$  will be used to differentiate the effective ethylene pressure from the system pressure. In effect, this term describes the ethylene pressure required at a specific temperature to reach the actual ethylene concentration in the liquid phase at saturation.

The pre-catalyst (metal precursor and ligand mixture) was activated with MMAO-3A prior to being introduced into the tubular reactor. The tubular reactor was operated isothermally at the

Table 1

Comparison of two different reactor concepts for the continuous oligomerization of ethylene with respect to specific requirements for ethylene oligomerization.

PFTR	CSTR
+ defined residence time distribution of catalyst molecules	– broad residence time distribution of catalyst molecules
+ higher selectivity to primary reaction products possible due to lower mean product concentration (and thus less secondary incorporation reactions)	– lower selectivity to primary reaction products due to higher mean product concentration (and thus more secondary incorporation reactions)
– heat removal at high reaction rates requires high flow rates leading to long reactors for a given residence time	+ effective heat removal possible, heat transfer coefficient can be influenced during operation
– higher probability of blockage due to fouling	+ lower probability of blockage due to fouling

desired reaction temperature. Samples were taken at the reactor outlet (E) before the solid by-products (polyethylene) and the gas phase (essentially un-reacted ethylene) were separated from the liquid solvent–product phase (H) in two sequential separators (F, G). The catalyst and solvent was fed to the reactor via HPLC-pumps (Latek P-402 40 ml/min and Knauer 10 ml/min, respectively). Temperature and pressure were measured at multiple points throughout the unit (see Fig. 2) and recorded by automated data acquisition software. The amounts of ethylene that both entered and exited the reactor were determined and controlled via coriolis mass-flow-controllers.

Due to the high sensitivity of this catalyst system to poisons (which includes air and moisture), the whole reactor unit was thoroughly cleaned prior to each run. Cleaning procedures employed include mechanical removal of polymer remains, overnight heating (120 °C) under reduced pressure and purging with inert gas (argon). During catalysis itself, samples were taken at regular intervals into cold glass tubes (pre-cooled to –18 °C to ensure a representative composition of the liquid phase by limiting the evaporation of low boiling components). The liquid solvent–product mixture was analyzed after filtration through cotton wool via GC on a Varian 3900 GC fitted with a CP Sil Pona CB 50 m × 0.21 mm column.

In general, two different reactor concepts, i.e. the plug flow tubular reactor (PFTR) and the continuous stirred tank reactor (CSTR) are used in industrial ethylene oligomerization processes [26]. The advantages (indicated by '+') and disadvantages (indicated by '–') of these two reactor concepts (PFTR and CSTR) are compared in Table 1.

The decision to use a PFTR for the main reactor in this study was mainly based on the fact that ethylene cost is a significant economic driver of any ethylene oligomerization process. Thus, high product selectivity is a key requisite to minimize ethylene loss by means of side-product formation. In the case of ethylene tri- and tetramerization, high primary product (1-hexene and/or 1-octene) concentration generally leads to increased secondary incorporation of these product(s) (see Fig. 3) to yield predominantly branched long-chain alkenes [9]. Consequently, when conducting such reactions in a PFTR, comparatively high primary product selectivity (1-hexene and/or 1-octene) can be expected due to the relatively low mean product concentration in the reaction solution. Having said this, the PFTR has to be operated with care during ethylene oligomerization reactions in order to minimize polymer fouling that would ultimately result in a complete reactor shut-down.

### 2.3. Calculating the overall mass balance for oligomerization reactions in the PFTR

Prior to conducting the individual catalytic runs, emphasis was placed on achieving a reliable mass balance for each oligomer-

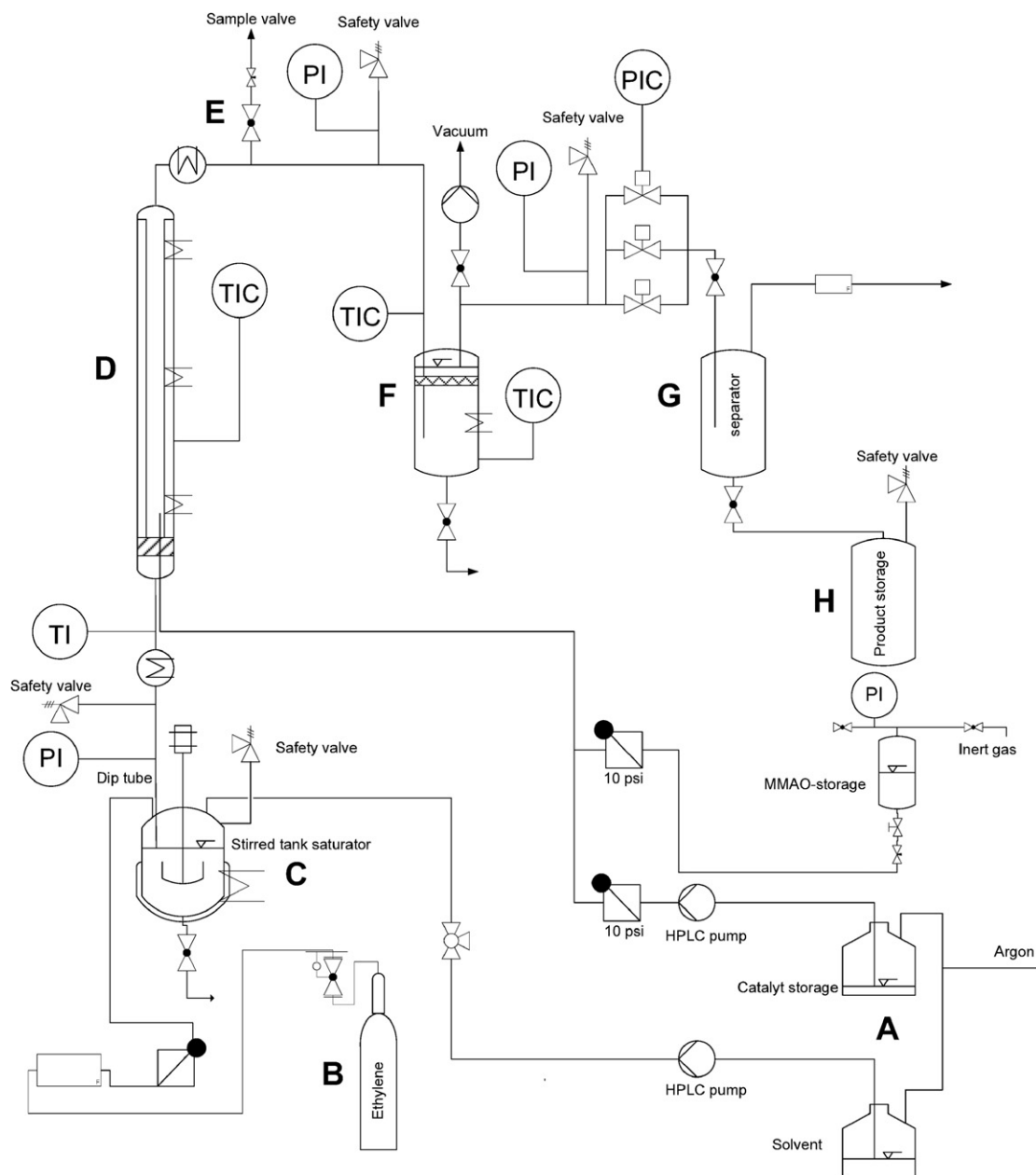


Fig. 2. Schematic set-up of the PFT reactor used in this study.

ization reaction (in the PFTR), thereby ensuring that correct and meaningful conclusions could be made by interpretation of run data. This exercise required accurate and independent determination of the mass of ethylene fed to the reactor, ethylene in the off-gas and in the solvent–product mixture. A simplified ethylene mass balance thus reads:

$$m_{C_2H_4, in} = m_{C_2H_4, out} + m_{liquid\ products} + m_{polymer}. \quad (1)$$

The ethylene feed and off-gas masses were conveniently determined via in-line coriolis mass-flow meters. The composition of the solvent–liquid product mixture was determined by GC as indicated above (the solvent was used as the internal standard to quantify individual components). The solid by-product was collected by filtration of the reaction mixture through filter paper, dried overnight at 100 °C and quantified. Two aspects which generally influence the accuracy of the ethylene mass balance are (a) the fact that the off-gas generally contains very small amounts of gaseous by-products (e.g., 1-butene, butane) in addition to the

ethylene, and (b) the fact that a small fraction of the ethylene remains dissolved in the liquid product phase without being detected by either the mass-flow meter at the reactor outlet or during analysis of the liquid phase (in other words it is lost due to evaporation before analysis of the liquid sample). Nevertheless, the ethylene mass balance given by Eq. (1) could be repeatedly closed within 2% over all samples of the 10 h experiments.

#### 2.4. Catalyst residence time distribution studies on the PFTR contents

Step function tracer experiments were conducted according to literature procedures [27] in order to study the catalyst residence time distribution (RTD) of the PFTR under investigation. These experiments were aimed at determining the Bodenstein number ( $Bo$ ), a dimensionless characteristic parameter that represents the ratio of forced convection ( $u \cdot L$ ) to axial dispersion  $D_{ax}$  within the PFTR:

$$Bo = \frac{u \cdot L}{D_{ax}}. \quad (2)$$

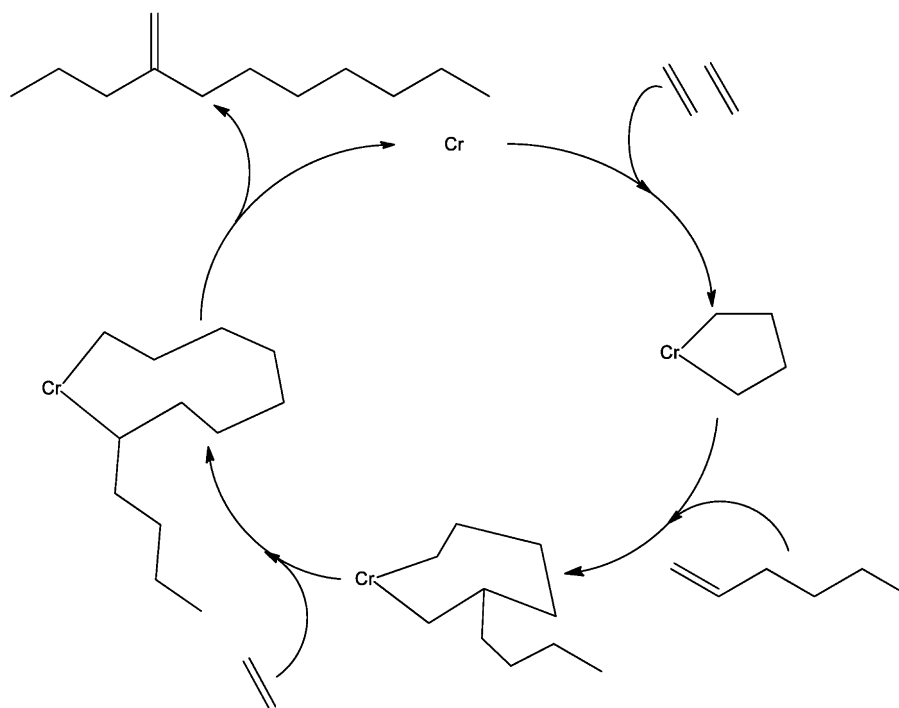


Fig. 3. Proposed secondary incorporation of higher olefins into the metallocycle reaction mechanism.

Table 2

Run parameters employed in the PFTR study.<sup>a</sup>

Entry	<i>T</i> (°C)	<i>c</i> (Cr) (μmol/L)	<i>c</i> (MAO) (mmol/L)	Al:Cr	Ethylene feed (g/min)	<i>p</i> <sub>effective</sub> (bar)
1	60	1...5	4.06	810...4050	3	25.9
2	60	3.5...10	4.06	405...1157	3	25.9
3	60	6.5	4.06	623	3, 5 <sup>b</sup>	25.9, 37.4
4	40, 50, 60	0.5	4.06	8100	3	25.9

<sup>a</sup> All runs were conducted in the continuous PFTR depicted in Fig. 2; solvent flow rate = 30 ml/min, *V*(reactor) = 600 ml, 16 min residence time, 50 bar overall pressure.

<sup>b</sup> The change in residence time due to higher ethylene feed rate was incorporated into the calculations.

For typical reaction conditions (60 °C, 50 barg ethylene pressure, solvent flow rate = 20 ml/min, average catalyst residence time = 30 min), a value of 616 was obtained. According to the literature [28] such a high *Bo* indicates that the RTD of the PFTR used in this study is comparable to a cascade of stirred tanks with more than 300 reactors in series. This indicates that little axial dispersion within the PFTR takes place under the applied conditions and that the obtained residence time distribution can be regarded as close to ideal plug flow behavior.

With the above-mentioned two important pre-requisites of an accurate mass balance and a close to ideal plug flow behaviour being met, several process parameters were subsequently evaluated using the PFTR (as summarized in Table 2).

### 2.5. Experimental set-up of semi-batch kinetic experiments

All kinetic experiments were carried out using a 450 ml Parr reactor which was fitted with (a) a gas-entrainment stirrer for optimum saturation of the liquid phase, (b) a burette for charging the catalyst under pressure, (c) an internal cooling coil coupled to an external cooling bath to maintain isothermic process conditions ( $\pm 1$  °C), (d) a sampling unit at the bottom of the autoclave for taking samples over the course of the reaction, (e) a Coriolis mass-flow meter for measuring ethylene consumption, (f) an inert

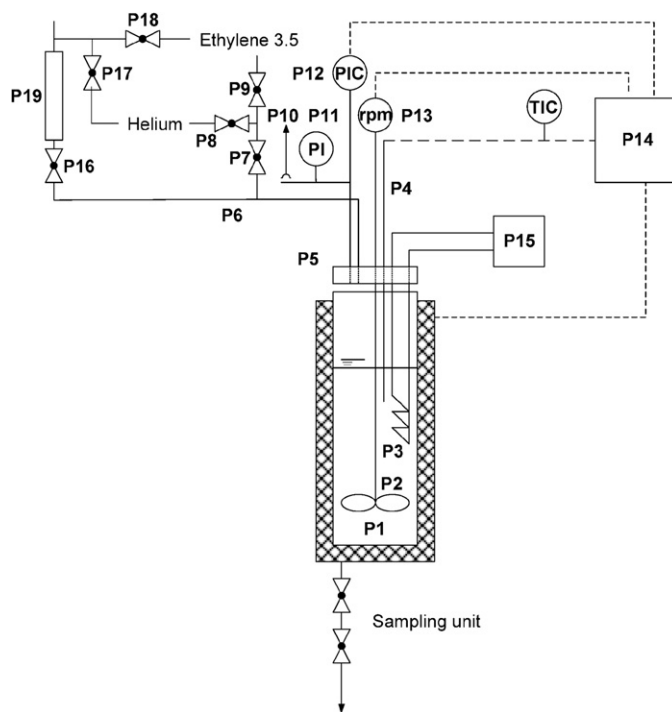
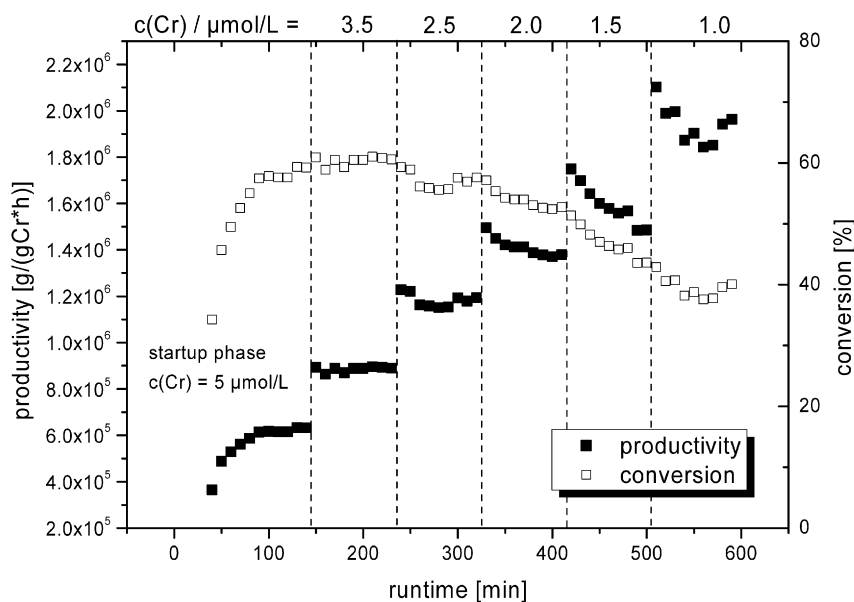


Fig. 4. Semi-batch reactor setup for kinetic studies.

gas-line (helium) and the ethylene feed line (see Fig. 4). Prior to reaction, the autoclave was cleaned thoroughly and heated to 120 °C under vacuum over night. The reactor was then cooled down under a helium atmosphere. A hot solvent wash using cyclohexane was carried out after every 5 runs to ensure the reliability and reproducibility of reaction data.

In order to guarantee the reliability of the collected data, a series of consecutive runs were carried out at fixed parameter settings. From the obtained product mass over time, the average catalyst activity could be calculated on a  $g/(g_{Cr} \cdot h)$  basis.



**Fig. 5.** Variation of chromium concentration—the effect on catalyst activity and ethylene conversion over time ( $c(\text{Al}) = 4.06 \text{ mmol/l}$ ,  $T = 60^\circ\text{C}$ ,  $p = 50 \text{ barg}$ ,  $p_{\text{effective}} \sim 26 \text{ bar}$ , see entry 1 in Table 2).

### 2.6. Experimental procedure of semi-batch tetramerization reactions

All catalytic runs were carried out according to the following procedure:  $2.5 \mu\text{mol Cr}(\text{acac})_3$  and an equimolar amount of the diphosphine ligand were taken from a prepared stock solution and transferred into a Schlenk-tube inside a glove box. Cyclohexane was added to increase the total volume to 5 ml. This solution was transferred immediately into a 450 ml autoclave containing 195 ml cyclohexane at the desired reaction temperature. The reaction vessel was then pressurized with ethylene to a pressure 5 bar below the desired run pressure. Next, the MMAO-3A activator solution was injected into a burette under helium atmosphere. This burette was then pressurized with ethylene to the desired run pressure. The reaction was initiated by injecting the MMAO-3A activator to the pre-saturated catalyst solution. Ethylene was fed on demand throughout the duration of the experiment. The reaction temperature was monitored via an internal thermocouple and maintained by an internal cooling coil connected to an external cooling bath. Samples were taken into pre-cooled glass vials ( $-18^\circ\text{C}$ ). The standard reaction time was chosen to be 30 min with samples being taken every 5 min. After 30 min, the reaction was terminated by closing the ethylene supply, switching off the gas entrainment stirrer and cooling the autoclave to  $0^\circ\text{C}$ . All liquid product samples were filtered and submitted for GC-FID analysis.

## 3. Results and discussion

### 3.1. Continuous miniplant runs—influence of chromium concentration ( $c(\text{Cr})$ )

From an industrial point of view, efficient utilization of the MMAO activated catalyst is an important pre-requisite for an economically attractive ethylene tetramerization technology. Thus, high reaction rates/activity (in terms of g product per g chromium per time interval) are desirable. In order to determine the minimum chromium concentration that still allows safe operation (e.g., with respect to polymer formation and reactor fouling), the catalyst feed rate was steadily decreased over time. Two such runs were carried out using the PFTR in which the catalyst concentration was varied from  $10 \mu\text{mol/l}$  down to  $1 \mu\text{mol/l}$ . A general trend

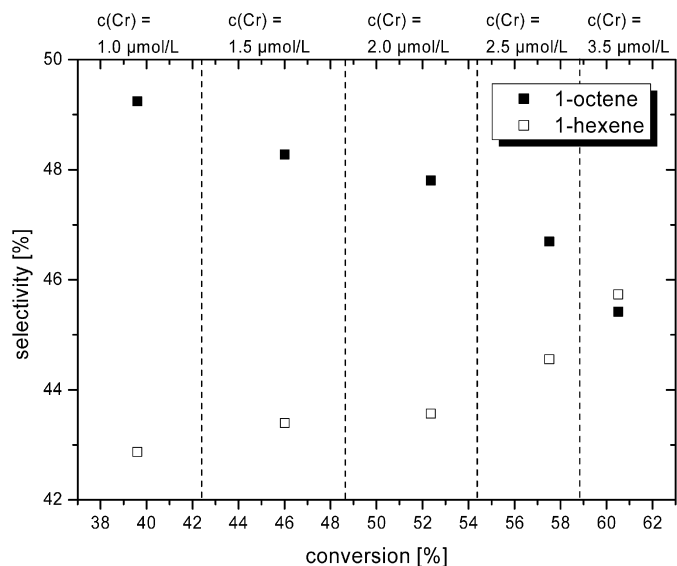
was expected in which the total ethylene conversion decreases with a decrease in the catalyst concentration.

During the first experiment the  $c(\text{Cr})$  was lowered stepwise from  $5 \mu\text{mol/l}$  down to  $1 \mu\text{mol/l}$ , while the aluminum concentration ( $c(\text{Al})$ ) of the activator MMAO-3A was kept at a constant level of  $4.06 \text{ mmol/l}$  throughout the duration of the experiment. Therefore, the Al:Cr molar ratio increased from 810:1 (for the 40–140 min run time period;  $c(\text{Cr})$  at  $5 \mu\text{mol/l}$ ) to 4050:1 (for the 510–600 min run time period;  $c(\text{Cr})$  at  $1 \mu\text{mol/l}$ ). As can be seen from Fig. 5 (see Table 2, entry 1 for experimental conditions), this change went hand in hand with a significant increase in activity. While the initial catalyst activity was around  $650,000 \text{ g}/(\text{gCr}\cdot\text{h})$  at a  $c(\text{Cr})$  of  $5 \mu\text{mol/l}$ , it increased stepwise to almost  $2,000,000 \text{ g}/(\text{gCr}\cdot\text{h})$  at a  $1 \mu\text{mol/l}$  concentration. Ignoring the non-steady state startup phase of the rig, after each drop in  $c(\text{Cr})$ , a steady-state condition with constant catalyst activity was clearly visible once the reactor contents had been displaced three times (after approximately 1 h).

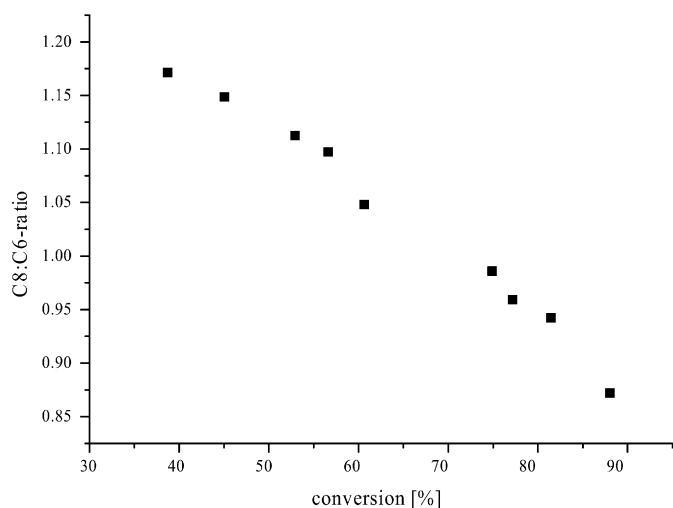
Although the gradual increase in the Al:Cr molar ratio in this experiment could at least be partly responsible for the increase in catalyst activity by allowing more effective activation of the catalyst complex, it is unlikely that this aspect is solely responsible for the dramatic improvement from  $650,000$  to  $2,000,000 \text{ g}/(\text{gCr}\cdot\text{h})$  obtained upon reducing the  $c(\text{Cr})$  from  $5$  to  $1 \mu\text{mol/l}$  which might suggest that the reaction order with respect to chromium concentration is unequal to one. A comparison with former studies carried out by Walsh et al. [23] and Hagen et al. [29], however, shows that this is improbable. Thus, it is believed that a second parameter, namely the difference in the mean ethylene concentration employed in the present PFTR experiment, is predominantly responsible for this trend (as will be elaborated upon below in Section 3.3). While the catalyst activity increases with decreasing catalyst concentration, the ethylene conversion follows the opposite trend. The ethylene conversion reaches its maximum of 60% at a  $c(\text{Cr})$  of  $3.5 \mu\text{mol Cr/l}$  during the first run period after the startup phase (Fig. 5, 140 to 240 min), and then drops consecutively in response to the stepwise decrease in the catalyst concentration down to only 40% at  $1 \mu\text{mol Cr/l}$  (Fig. 5, 510 to 600 min).

Most notably, the ethylene conversion also seems to have a strong influence on the reaction product selectivity as shown in Fig. 6. At a 40% ethylene conversion (obtained at  $1 \mu\text{mol/l}$





**Fig. 6.** Product selectivity as a function of ethylene conversion ( $c(\text{Al}) = 4.06 \text{ mmol/l}$ ,  $T = 60^\circ\text{C}$ ,  $p = 50 \text{ barg}$ ,  $p_{\text{effective}} = 25.9 \text{ bar}$ , see entry 1 in Table 2).



**Fig. 7.** Primary product distribution as a function of ethylene conversion; data from two consecutive runs ( $c(\text{Al}) = 4.06 \text{ mmol/l}$ ,  $T = 60^\circ\text{C}$ ,  $p = 50 \text{ barg}$ ,  $p_{\text{effective}} = 25.9 \text{ bar}$ , see entries 1 and 2 in Table 2).

chromium concentration) the 1-octene selectivity exceeds 49% with the 1-hexene selectivity at 42.5%. With an increase in ethylene conversion up to its maximum at 60% (obtained at 3.5  $\mu\text{mol/l}$  chromium concentration), the 1-octene selectivity decreases correspondingly to less than 46% in favor of 1-hexene.

To prove this dependence at even higher levels of total ethylene conversion, an analogous run to the first experiment at a constant  $c(\text{Al})$  of 4.06  $\text{mmol/l}$  was conducted in which the chromium concentration was systematically reduced from 10 to 3.5  $\mu\text{mol/l}$  (and correspondingly the Al:Cr molar ratio from 405:1 to 1157:1, see entry 2 in Table 2). It is clearly evident that there is further decrease of the 1-octene to 1-hexene ratio up to a total ethylene conversion of 90% (see Fig. 7).

It is also worth mentioning that the ratio of 1-octene to 1-hexene never exceeded 1.3:1 in both the PFTR runs, which is markedly lower than the usual ratio obtained in batch reactions with the same catalyst (2.7:1). However, since 1-octene selectivity is favored by high ethylene concentrations, this observation is to be expected given that the mean ethylene concentration in the

**Table 3**

Variation of reaction temperature—effect on activity, ethylene conversion and primary product selectivity.<sup>a</sup>

$T$ ( $^\circ\text{C}$ )	Activity ( $\text{g}/(\text{g}_{\text{Cr}} \text{ h})$ )	Conversion (%)	Selectivity (%)	
			1-C <sub>6</sub>	1-C <sub>8</sub>
40	$1.2 \times 10^6$	9.2	18.5	62.7
50	$2.3 \times 10^6$	17.9	26.8	58.5
60	$3.7 \times 10^6$	22.1	39.5	50.1

<sup>a</sup> See Table 2, entry 4 for details on reaction conditions.

PFTR (which decreases across the length of the reactor) is lower than in a CSTR which is operated at a constant pressure.

Finally, it also has to be noted that the combined yield of 1-hexene and 1-octene remained constant at 91...92 wt% throughout these two experiments which is in agreement with the reported semi-batch reaction results of Kuhlmann et al. with a very similar catalyst [24]. It is also in good accordance with the 86.1 wt% reported for a semi-batch tetramerization reaction (ethylene fed on demand at a constant reaction pressure) using the same catalyst system and reaction conditions [14].

### 3.2. Continuous miniplant runs—influence of temperature

Previously, semi-batch ethylene tetramerization experiments showed that the ratio of 1-octene to 1-hexene is profoundly influenced by changes to the reaction temperature [24]. Since the ratio of these two products would influence both the design and economic performance of a commercial ethylene tetramerization production unit, it was thus decided to also study the influence of reaction temperature on both reaction selectivity and catalyst activity in the continuous PFTR. The run parameters for this study are given in Table 2, entry 4; the results are summarized in Table 3.

With respect to the dependence of catalyst activity on reaction temperature, a decrease in temperature from 60  $^\circ\text{C}$  to 50  $^\circ\text{C}$  and further to 40  $^\circ\text{C}$  resulted in drastic reduction in reaction rate. While an activity of  $3.7 \times 10^6 \text{ g}/(\text{g}_{\text{Cr}} \text{ h})$  could be realized at 60  $^\circ\text{C}$ , it dropped to  $2.3 \times 10^6 \text{ g}/(\text{g}_{\text{Cr}} \text{ h})$  at 50  $^\circ\text{C}$  and even further to  $1.2 \times 10^6 \text{ g}/(\text{g}_{\text{Cr}} \text{ h})$  at 40  $^\circ\text{C}$ . This reaction temperature–reaction activity trend is also in good accordance with the observations by Walsh et al. in semi-batch ethylene tetramerization experiments [23]. It is noteworthy that the observed catalytic activity at 60  $^\circ\text{C}$  in this experiment is significantly higher than in two runs reported above ( $3.7 \times 10^6 \text{ g}/(\text{g}_{\text{Cr}} \text{ h})$  vs. roughly 2,000,000, see Fig. 5). It is believed that this increase can exclusively be attributed to the higher mean ethylene concentration in the reactor caused by the lower total ethylene conversion, which in turn is a result of the lower catalyst concentration employed in this experiment (0.5  $\mu\text{mol/l}$  instead of 1  $\mu\text{mol/l}$ , see Table 2).

The influence of temperature on reaction selectivity was also consistent with both the aforementioned batch studies [14,24]. From Table 3 it is evident that a decrease in reaction temperature led to a significant increase in 1-octene formation (50.1% 1-octene at 60  $^\circ\text{C}$  vs. 62.7% 1-octene at 40  $^\circ\text{C}$ ). This trend of increased 1-octene formation was accompanied by a simultaneous drop in 1-hexene formation from 39.5% to less than 20% upon going from 60 to 40  $^\circ\text{C}$ . The combined yield of 1-octene and 1-hexene stayed roughly constant in the 85–90 wt% range throughout the duration of this experiment.

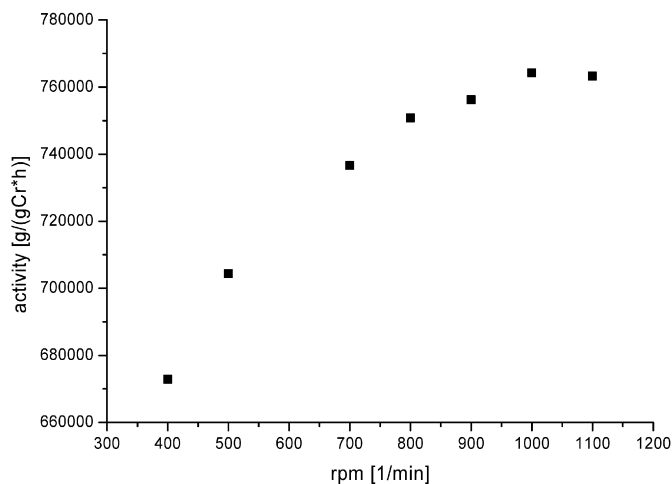
### 3.3. Continuous miniplant runs—influence of ethylene concentration

Due to the high activity of the catalyst system employed in this study, it is very likely that  $c(\text{ethylene})$  decreases quickly along the length of the reactor tube with the most of the solubilized ethylene being consumed over the first section of the reactor length. Assuming that this oligomerization reaction has a 1.57 order dependence

**Table 4**  
Variation of ethylene feed rate—effect on product selectivity and ethylene conversion.<sup>a</sup>

Ethylene feed (g/min)	$p_{\text{effective}}$ (bar)	Selectivity (%)		$C_8:C_6$ ratio	Conversion (%)
		1- $C_6$	1- $C_8$		
3	25.9	48.9	38.2	0.78	82.5
5	37.4	37.3	48.2	1.29	85.8

<sup>a</sup> See Table 2, entry 3 for detailed reaction conditions.



**Fig. 8.** Catalytic activity as a function of the stirrer speed ( $T = 60^\circ\text{C}$ , 45 bar ethylene pressure,  $c(\text{Cr}) = 12.5 \mu\text{mol/l}$ , Al:Cr ratio = 480).

on  $c(\text{ethylene})$  (as reported by Walsh et al. [23]), this rapid decrease in  $c(\text{ethylene})$  would result in an even faster decrease in the reaction rate over the reactor length. One can thus assume that the relative quantity of product formed at lower  $c(\text{ethylene})$  during the later part of the reactor length and its subsequent contribution to the overall reaction selectivity would therefore be less significant.

In the light of the reaction pressure–reaction selectivity trends observed in the aforementioned batch studies where increasing the ethylene pressure generally leads to increased 1-octene formation [14,24], it thus should be possible to achieve a higher selectivity towards 1-octene in the PFTR at a given reaction temperature and  $c(\text{Cr})$  by increasing the overall amount of ethylene entrained into the solvent phase (if the above assumption is indeed correct). To study this effect an experiment was carried out on the PFTR in which the ethylene concentration in the solvent at the reactor inlet was varied (see entry 3 in Table 2). During this run, the catalyst concentration as well as all other parameters except for the ethylene feed rate were kept constant for the duration of the run. It should be noted that due to volume increase of the solvent–ethylene phase, the actual catalyst residence time was lower at higher ethylene feed rates. However, since the overall ethylene conversion at the reactor outlet was similar (82.5% at 3 g/min vs. 85.8% at 5 g/min) for both data points, it is still valid to compare the obtained product selectivities.

From the data in Table 4 it is evident that, as expected, by increasing the ethylene concentration at the reactor inlet the overall product selectivity at the reactor outlet shifted from predominantly 1-hexene formation (48.9% 1- $C_6$  and 38.1% 1- $C_8$ ) to 1-octene formation (37.3% 1- $C_6$  and 48.2% 1- $C_8$ ). The 1- $C_8$ :1- $C_6$ -ratio thereby increases by 65% from 0.78 to 1.29.

In an attempt to elucidate this selectivity behavior, more detailed studies on the influence of ethylene concentration on product selectivity were carried out in semi-batch mode using the reactor set-up described above in Fig. 4 (see Section 3.4).

### 3.4. Semi-batch kinetic investigation to study the rate of formation of 1-hexene and 1-octene individually with respect to ethylene concentration

In order to eliminate any ethylene mass transfer considerations during the collection of the actual kinetic data, this study was initiated by varying the stirrer speed from 400 to 1100 rpm at constant temperature and pressure (60 °C and 45 barg) to determine the stirring rate at which the reaction is free of any significant mass transfer effects.

Fig. 8 indicates that increasing the stirrer speed from 400 to 1000 rpm leads to an increase in catalytic activity (670,000 to 760,000 g/(gCr h)). Increasing the stirrer speed beyond 1000 rpm did not provide further catalyst activity improvements which is evidence for a stirring speed regime where no more mass transfer limitation hinders the reaction rate. Thus, all subsequent kinetic runs were performed at a stirrer speed of 1200 rpm.

Our motivation to carry out the more detailed kinetic investigation presented in this paper was twofold in nature: (a) to gather more detailed information on the influence of ethylene concentration on the selectivity of the main products 1-octene and 1-hexene (as indicated above); and (b) to compare the kinetic data for this more optimized catalyst system (DMP-PNP/Cr(acac)<sub>3</sub>/cyclohexane/MMAO-3A, see Fig. 1) with that reported for the “first generation” iso-propyl-PNP/Cr(acac)<sub>3</sub>/cumene/MAO catalyst [23].

We chose the power rate law approach for the development of a kinetic expression (Eqs. (3) and (4)) to allow a direct comparison of this expression with available data from the literature. Since the reaction dependence on metal concentration has been reported to be first order for both chromium and titanium based selective oligomerization catalysts [23,29], we chose not to investigate this parameter further.

$$r = \frac{dm_{\text{product}}}{dt} = k \cdot [C_2H_4]^n, \quad (3)$$

$$k = k_0 \cdot \exp\left(\frac{-E_A}{RT}\right). \quad (4)$$

The reaction rates ( $dm_{\text{product}}/dt$ ) of reactions conducted at different pressures were obtained from the GC data of samples taken over the course of these reactions (total run time of 30 min with samples being taken at 5 min intervals). Thus, the amount of liquid product formed over time could be calculated and the rate of product formation obtained by determining the slope  $\Delta m_{\text{product}}/\Delta t$  (taken as the rate in g/h) for each reaction. This seemed to be the most accurate and convenient route for establishing the reaction rates, as it allowed maximum reliability and reproducibility. In contrast, monitoring either pressure decay or ethylene uptake both have the inherent disadvantage that no information on the liquid composition of the reaction mixture can be gathered over time.

The reaction order with respect to ethylene could now be determined from the slope of a  $\ln(\text{rate})$  versus  $\ln(\text{pressure})$  plot. Although the composition of the liquid phase changes during the course of the reaction due to product formation, the corresponding gradual change in ethylene solubility was neglected in our calculations. In our kinetic experiments, the end-of-run product concentration was relatively low (representing maximum 10–15 wt% of the solvent–product mixture), thereby implying that a negligible error would be realized by ignoring the change in ethylene solubility.

Thus, after establishing both a regime in which the reaction was free of any mass transfer limitations and reaction reproducibility, the kinetic parameters were established by varying the reaction pressure (15–45 barg) at a fixed temperature (60 °C). 2.5  $\mu\text{mol}$  Cr(acac)<sub>3</sub> and 200 ml solvent was employed in each run, thus giving an initial chromium concentration of 12.5  $\mu\text{mol/l}$  Cr (prior to

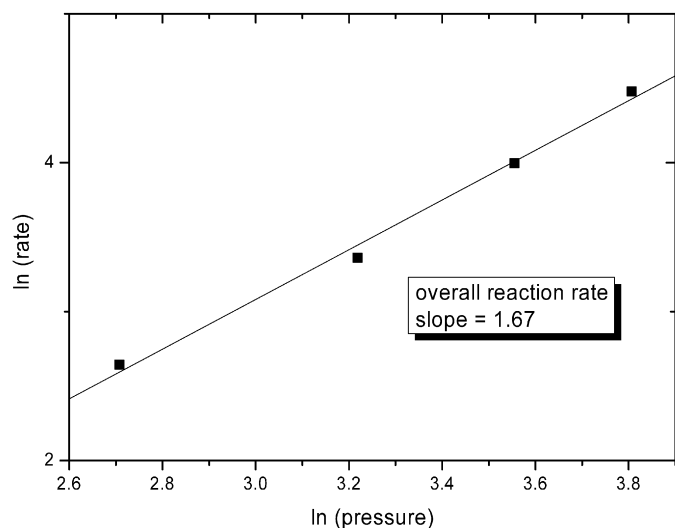


Fig. 9. Overall reaction order for the combined tri- and tetramerization with respect to ethylene concentration.

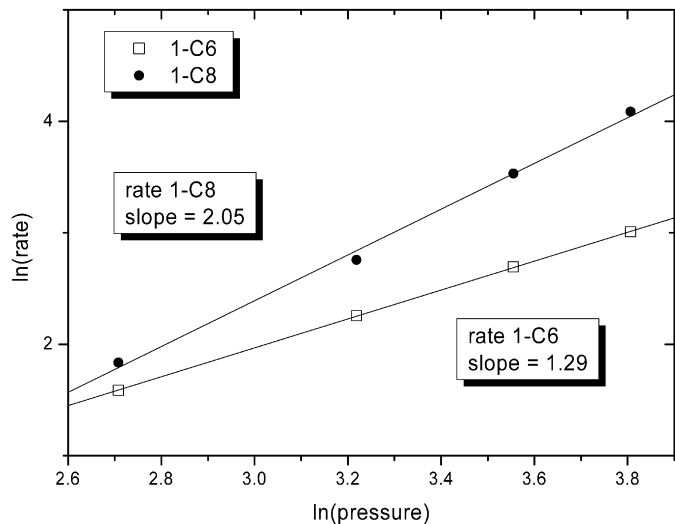


Fig. 10. Individual reaction orders for 1-hexene and 1-octene with respect to ethylene concentration.

ethylene saturation). Physical property data that was published recently by our group shows that there is a strong linear correlation between ethylene pressure and ethylene liquid phase concentration [24]. Hence, from the slope of the  $\ln(\text{rate})$  versus  $\ln(\text{pressure})$  plot it was determined that the overall reaction order with respect to ethylene was 1.67 (see Fig. 9). This is in good agreement with the studies carried out by Walsh et al., where the reaction order was found to be 1.57 [23].

This fractional reaction order over the 15–45 barg ethylene pressure range suggested the existence of at least two concurrent reaction pathways, each with its own rate determining step (possibly with integral reaction orders). In order to study this possibility further, the ethylene concentration dependence for the formation of the two main products (1-octene and 1-hexene) were plotted individually (see Fig. 10). Thereby, it became evident that the rate of formation for 1-octene follows a higher order (2.05) than the rate of formation for 1-hexene (1.29). Notably, integral reaction orders were not obtained for the DMP-PNP system as anticipated. The exact reason for this remains unclear; error analysis on ethylene order shows deviations of  $\pm 15\%$  which includes the possibility for ethylene order to 1-hexene to be 1, and ethylene order to 1-o-

tene to be 2. A possible explanation of the significant difference in reaction order arises from the fact that, after the initial oxidative coupling of two ethylene molecules (according to the proposed mechanism by Overett et al. [18]), the formation of 1-octene demands further insertion of two ethylene molecules while 1-hexene formation needs only one additional ethylene.

Nevertheless, the significant difference in the reaction orders for both main products still provides an adequate explanation for the product selectivity dependence on ethylene concentration as observed during the continuous PFTR runs. In order to evaluate the relevance of these data with respect to selectivity optimization, refining of the current mechanistic understanding will be necessary.

#### 4. Conclusions

This paper provides the first documented study on the continuous selective tri- and tetramerization of ethylene with an aluminum-activated chromium catalyst in a PFTR. Process parameter variation studies showed that the ratio of 1-octene:1-hexene can be shifted towards 1-octene by lowering the reaction temperature. Furthermore, increasing the amount of ethylene available in the solvent phase by entraining more ethylene and lowering the total ethylene conversion, respectively, led to higher reaction rates as well as reduction of the 1-hexene selectivity in favor of the 1-octene selectivity.

A combined selectivity for 1-hexene and 1-octene exceeding 90% with activities in excess of 3,700,000  $\text{g}/(\text{g}_{\text{Cr}} \text{h})$  was achieved. The mass balance over the whole 8–10 h reactions (including the formation of polymers) was repeatedly closed within 2%. Kinetic studies in a semi-batch reactor setup revealed that rate of formation for the two main products have different orders with respect to ethylene concentration, which gives an adequate explanation for the observed shifts in reaction selectivity as a result of changes to the reaction parameters.

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