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Oligomerisation of linear 1-olefins using a chlorogallate(III) ionic liquid*

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Abstract: A Lewis acidic chlorogallate(III) ionic liquid, 1-ethyl-3-methylimidazolium heptachlorodigallate(III), $[C_2mim][Ga_2Cl_7]$, was successfully used to oligomerise 1-pentene. The influence of temperature, time, catalyst concentration, and stirring rate on conversion and product distribution was modelled using a design of experiment (DoE) approach (chemometrics). The process was optimised for lubricant base oils production; the C20–C50 fraction (where *Cn* indicates the number of carbons in the oligomer) was maximised, while the heavier oligomer fraction (>C50) was minimised.

Keywords: 1-alkenes; chemometrics; ionic liquids; linear terminal olefins; 1-olefins; oligomerisation.

INTRODUCTION

Oligomerisation and ionic liquids

Polyalphaolefins (PAOs), used as a base for synthetic automotive lubricants (Group 4 base stock by API classification) [1], are traditionally made by oligomerisation of 1-decene to C20–C50 blend (where Cn indicates the number of carbons in the oligomer) [2] using Ziegler–Natta or Friedel–Crafts catalysts [3]. The carbon number is important, as the pour point of higher polymers (>C50) is too high, whilst the lower cut (<C20) is too volatile. 1-Decene is manufactured in a very selective manner from ethene [2]. Currently, the high price of ethene (ca. \$1000 t⁻¹) has resulted in the high price of 1-decene (ca. \$1700 t⁻¹). Since the market price of PAOs is about \$1800 t⁻¹, its manufacture from 1-decene is unlikely to be profitable. At the same time, lower 1 α -olefins from a refinery or petrochemical plant are inexpensive and abundant**, e.g., pentenes cost around \$203 t⁻¹ [4]. This encourages a search for inexpensive methods to convert lower α -olefins to PAOs.

Ionic liquids are compounds composed exclusively of ions—usually a bulky organic cation and an organic or inorganic anion—which results in a good solvating ability and very low volatility [5]. The first ionic liquids to be tested for oligomerisation processes were chloroaluminates(III) [6]. They are prepared by mixing aluminium(III) chloride and an organic chloride salt [7]. Depending on the reagent ratio (expressed as the nominal mol fraction of aluminium(III) chloride, χ_{AlCl3} , the ionic liquids formed may be Lewis basic due to the presence of a chloride anion (for $\chi_{AlCl3} < 0.5$), neutral (for

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^{**}Whereas PAOs can be made only from expensive 1-decene, an inexpensive mixture of pentenes can be used on an industrial scale to prepare their equivalents, polyinternalolefins (PIOs).

 $\chi_{AlCl3} = 0.5$), or acidic (for $\chi_{AlCl3} > 0.5$). For $\chi_{AlCl3} > 0.67$, chloroaluminate(III) systems no longer form homogenous ionic liquids, but aluminium(III) chloride precipitates out as a white powder. Aside from being strong Lewis acids (in appropriate compositions) [8], chloroaluminate(III) ionic liquids are good solvents for metal complexes and at the same time poor solvents for hydrocarbons [9]. These properties allowed their use in oligomerisation processes, either as solvents and/or as co-catalysts (in Lewis acidic [10] or buffered to neutral [11] form) in metal complex-catalysed reactions, or as catalysts in their own right—be it Lewis acidic catalysis, or as part of a Brønsted superacidic system [12]. Besides the peer-reviewed literature, a number of patents regarding oligomerisation and similar processes using chloroaluminates was filed [13,14]. However, chloroaluminate(III) ionic liquids are extremely moisture-sensitive [7,15] and hydrolyse to release hydrogen chloride in contact with traces of water. This poses serious safety concerns for the process scale-up, and affects reproducibility of the results. Furthermore, used as Lewis acidic catalysts, they tend to be extremely active in promoting not only cationic oligomerisation, but also isomerisations, thus often producing highly branched polymers (even if oligomers would be preferred) [11].

In a search of alternative media, other chlorometallate(III) systems were tested. For example, chloroferrate(III) ionic liquids, which are both moisture-stable [16] and Lewis acidic due to the presence of $[Fe_2Cl_7]^-$ in some compositions [17], were used for oligomerisation of isobutene to C8–C20 olefins [18]. The much lower Lewis acidity of the neat chloroferrate(III) systems, compared to the chloroaluminate(III) ones, manifested itself in a very moderate conversion (up to 11 wt %). However, introduction of a protic cation (and thus generation of a strong Brønsted acid) and furthermore addition of copper(I) oxide, increased conversion to 98 wt % [18].

Chlorogallate(III) ionic liquids have been known since 1987 [19], but their applications focussed mainly on electrodeposition [20,21], with very few examples in catalysis. The neutral chlorogallate(III) ionic liquids were used as solvents for palladium-catalysed hydroethoxycarbonylation [22] and acetal formation [23] (in the latter case, lack of atmospheric protection may have affected results), while a chlorogallate(III)-based Brønsted superacidic system was tested for arene carbonylation [24]. This lacuna is surprising, as chlorogallate(III) ionic liquids have several advantages over the aluminium(III)-based ones. Whereas the chloroaluminate(III) systems yield homogenous ionic liquids up to $\chi_{AlCl3} \leq 0.67$, the chlorogallate(III) ones do so for up to $\chi_{GaCl3} \leq 0.75$ [8]. Lewis acidity of chlorogallate(III) systems was demonstrated to be the same, or even higher ($\chi_{GaCl3} > 0.67$), than that of the analogous relevant chloroaluminates(III) [8]. At the same time, chlorogallate(III) ionic liquids appear to be much more resistant to hydrolysis than the chloroaluminate(III) ones [25].

The aim of this work was to test a chlorogallate(III) ionic liquid—a safer and more stable alternative to chloroaluminate(III) systems—as a catalyst for oligomerisation of olefins, with an objective to produce lubricant base oils (C20–C50) from an inexpensive 1-olefin feedstock (1-pentene). In order to optimise conversion and distribution of products, a DoE approach was adopted.

Design of experiments (DoE)

Investigating the influence of various factors (process variables) on a chemical process, traditional scientific methods involve planning of experiments in a rather unproductive way—one factor at a time (OFAT), often with several repetitions for every experiment. In contrast, the DoE methodology [26] involves investigating many factors in parallel via matrix-based test plans.

The most basic DoE design, 2^k , involves testing k factors on two levels (low and high, usually coded -1 and +1), so that for three factors with four repetitions the experimental matrix requires only $2^3 = 8$ experiments. The difference between the OFAT and DoE approaches is shown in Fig. 1. More advanced models of DoE exist, and these are summarised well elsewhere [26].



Fig. 1 Comparison of a 2^k (k = 3) factorial design (left) vs. OFAT (right) [26b].

Results obtained from a DoE approach may be statistically analysed using regression analysis and analysis of variance (ANOVA), and optimised using the response surface methodology (RSM) [27].

For a chemical process, the DoE approach usually comprises the following steps:

- Factors influencing the reaction are chosen (e.g., temperature, pressure).
- A DoE model is chosen.
- The experimental matrix is generated using a DoE software.
- The experiments are carried out in a strictly defined order (the order is randomised by the software to decrease the experimental error).
- Responses—"outcomes" of the experiments—are measured; for a chemical reaction, a response may be, e.g., yield, selectivity, or product viscosity.
- Responses are fed back to the DoE software.
- For every response, a mathematical model is constructed, showing the value of the response as a function of the factors (e.g., yield depending on time and temperature of the reaction); significance of the factor (e.g., whether pH variation affects the selectivity of a reaction, or is the effect within the error bars); and interactions between factors (e.g., synergies) are included in the model.
- Optimisation is carried out: responses may be minimised, maximised, or an optimum range of values can be determined; values of factors for the optimum response value are calculated.

Noteworthy, when a model is created, and the experimental matrix is generated, it is a purely mathematical process, and it operates on the coded values, with the minimum value of a factor coded as -1 and the maximum as +1 (see Fig. 1). Afterwards, it is up to the experimenter to assign meaning-ful physical values to the coded values—these are called actual values. As a result, from a relatively small number of experiments, it is possible to obtain a very useful model of key parameters of the process and their influence on the outcome (including possible synergies). This facilitates optimisation of the process by determining targets for several responses in parallel.

In this work, a central composite design (CCD) model [26a], based on the factorial design 2^k , was chosen, since it permits the fitting of a second-order model to the responses, whereas a standard 2^k design assumes linear interactions between factors. This type of experimental design consists of three types of experimental runs: factorial points (on the -1 and +1 level), central points improving precision of the model (medium level 0), and axial points allowing detection of quadratic effects (on the $-\alpha$ and $+\alpha$ level), as shown in Fig. 2. Importantly, introduction of the α values improves the model, but the response surface (model of the response values for given factor values) is modelled only within the -1 to +1 area.



Fig. 2 Experimental points for a CCD for three factors; two axial points (on the factor C axis) are not shown for clarity [26a].

EXPERIMENTAL

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich. 1-Pentene (99 %) was dried (for a minimum of 12 h) over 4 Å molecular sieves and stored under nitrogen gas. Gallium(III) chloride (anhydrous beads, 99.99 %) was purchased in sealed ampoules, opened, and stored in the glovebox. 1-Ethyl-3-methylimidazolium chloride was received from Accelergy. Calibration standards for SimDis GC, "Boiling Point Kit #2" and "Polywax 665", were purchased from Agilent.

Synthesis of 1-ethyl-3-methylimidazolium heptachlorodigallate(III), [C₂mim][Ga₂Cl₇]

In a glovebox, $[C_2mim]Cl$ (1.0 equiv, 2.3941 g, 0.0163 mol) was placed in a glass bottle (25 cm³) equipped with a stirring bar and stirred vigorously at room temperature. Gallium(III) chloride (2.0 equiv, 5.7504 g, 0.0327 mol) was added in small portions over 20 min, whence an exothermic reaction occurred immediately. When the addition was complete, the mixture was stirred vigorously (3 h) in the bottle, closed with a chemically resistant, poly(tetrafluoroethylene) (PTFE)-lined cap. A transparent, pale yellow ionic liquid was obtained in a 100 % (8.1445 g) yield.

Oligomerisation experiments

Reactor system

All oligomerisation reactions were carried out in glass H.E.L. AutoMATE LP batch reactors, each equipped with an overhead stirrer, fitted with two PTFE septa (for sampling and introducing the catalyst) and connected to the nitrogen gas line. The temperature in each reactor was measured by a thermocouple, and maintained by an internal heating wire and an external cooling mantle for precise temperature control. A battery of four computer-controlled reactors (50 cm³ each) permitted multiple simultaneous experiments.

Reaction procedure

The reactors were oven-dried, assembled still hot, purged with dry nitrogen gas (20 min), and then sealed. The glass syringes were dried overnight in the oven and cooled in a desiccator. The micro-syringes were dried by purging with dry nitrogen gas (10 min) and stored in a desiccator.

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1-Pentene was added to the reactor using a syringe, and stirred vigorously (1000 rpm) in order to equilibrate to the pre-set temperature. The ionic liquid was loaded in the glovebox to a dry microsyringe with a stainless steel needle. The syringe was sealed, removed from the glovebox, and immediately plunged into the reactor; the ionic liquid was added rapidly (in one step) to the stirred olefin. In all cases, a strongly exothermic reaction occurred. After a specified reaction time (from the ionic liquid addition), the reactor was opened and the reaction was quenched by stirring with rapidly added deionised water (10 cm³, 1000 rpm, ambient temperature, 20 min). When stirring stopped, the mixture separated into organic (top) and aqueous (bottom) layers. The ionic liquid had transferred completely to the aqueous layer, with no hydrocarbons detectable in this layer, as confirmed by ¹H NMR spectroscopy. The organic product was decanted to a pre-weighed round-bottomed flask (50 cm³) and weighed immediately. 1-Pentene (and possible isomers produced in the course of the reaction) were then removed using a rotary evaporator (room temperature, 30 min), and the conversion to oligomers was calculated. The products were analysed using the SimDis GC. Chromatograms and simulated distillation curves for all samples were compared. The mass percentages of desired oligomers (C20–C50) and of the high boiling end (undesired oligomers >C50) were calculated and compared.

The preliminary oligomerisation of 1-pentene (20 g, 1.00 equiv, 0.28 mol) with $[C_2mim][Ga_2Cl_7]$ (1.07 × 10⁻³ equiv, 0.149 g, 0.299 × 10⁻³ mol) was carried out at: 0 and 20 °C, 60 min, 1000 rpm. Quantities and conditions used for oligomerisation of 1-pentene according to DoE methodology were a part of the experimental design, and are therefore a part of the discussion section.

Simulated distillation—SimDis GC

All analyses were performed using an Agilent 6890N GC, equipped with a flame ionisation detector (FID) and a high-performance HT PTV inlet with optimised design for SimDis applications. An Agilent J&W DB-HT SimDis Column was used. Results were analysed using Agilent SIMDIS [28] software.

Calibration, validation, and sample testing methods were carried out according to the ASTM D6352 standard [29]. Modifications included: replacement of carbon disulfide with heptane (for health and safety reasons), and addition of triacontane and tetracontane to a standard calibration sample (comprising of "Boiling Point Kit #2", "Polywax 665", and eicosane) to facilitate peak identification. The validation sample was provided by Castrol. Each sample was studied as a diluted solution in heptane (ca. 2 wt %).

Design of experiment (DoE)

DoE was carried out with the aid of Design Expert 7.1³⁰ software.

RESULTS AND DISCUSSION

Preliminary oligomerisation experiment

Preliminary tests involved oligomerisation of 1-pentene at two temperatures, 0 and 20 °C, using catalytic amounts of $[C_2mim][Ga_2Cl_7]$. Reaction conditions, conversions and product distributions for the two test reactions catalysed by $[C_2mim][Ga_2Cl_7]$ are shown in Table 1.

Table 1 Temperatures, conversions and distributions for the oligomerisation of 1-pentene using $[C_2mim][Ga_2Cl_7]$. Reaction conditions: 60 min, 1000 rpm, 0.107 mol % of the catalyst.

#	Temperature	Conversion/%	Products distribution/%				
			C10 and C15	C20–C50	>C50		
I	0	2.5 ± 0.4	17 ± 1	59 ± 4	24 ± 2		
Π	20	6.0	22	58	20		

Chromatograms of products I and II are compared in Fig. 3. The first peak, ca. 180 °C, corresponds to all 1-pentene dimers (C10); the second peak, ca. 220 °C, to all the trimers (C15), etc. The higher the degree of oligomerisation, the more isomers are present. Since each isomer has a slightly different boiling point, they integrate to produce broad "humps" in the chromatogram.



Fig. 3 SimDis chromatograms of the products of reactions I and II.

In order to test reproducibility, reaction I was repeated two more times. An averaged distillation curve for the three studies of reaction I (with error bars indicating good reproducibility), and a distillation curve for reaction II, are shown in Fig. 4. A single distillation curve for reaction II has distinctive "steps" corresponding to dimers, trimers, etc. of 1-pentene, distilling at different temperatures.

The preliminary experiments showed good reproducibility and gave a high ratio of C20–C50 oligomers; unfortunately, in both cases the conversion was very low (Table 2). Predictably [31], the rise of temperature from 0 °C (reaction I) to 20 °C (reaction II) increased conversion, and at the same time gave shorter oligomers. Nevertheless, achieving a reasonable conversion by further temperature increase (without high-pressure reactors) is limited by the boiling point of 1-pentene (30 °C).

In such a situation, considering that conversion and products distribution are affected by a number of process variables (e.g., reaction time or concentration of a catalyst), it is beneficial to attempt optimisation adopting a DoE approach. Experimental design offers mathematical tools to model how conversion and oligomer distribution are affected by the process variables, as well as tools to optimise those variables, with only a limited number of experiments required. Using the DoE model, it is possible to understand the process, and estimate whether, with the given catalyst and feedstock, it is possible to achieve a satisfactory output.



Fig. 4 Simulated distillation curves of products of reactions I (solid curve with error bars, average of three experiments) and II (dotted curve). The dashed lines contain the desirable C20–C50 product range, corresponding to 350–575 °C boiling point ranges.

Variable	Status	Values
Engineering variables		
Reaction time/min	Variable	0 to 100
Temperature/°C	Variable	-5 to 21
Pressure	Fixed	Atmospheric
Stirring/rpm	Variable	500 to 1500
Volume of reaction mixture/cm ³	Fixed	30
Nature of reactor	Fixed	H.E.L. reactor (batch)
Chemical variables		
Olefin feedstock	Fixed	1-Pentene
Presence of a solvent	Fixed	No solvent
Catalyst concentration/mol %	Variable	0.00 to 0.60
Ionic liquid-related variables		
Cation	Fixed	[C ₂ mim] ⁺
Metal in anion	Fixed	Ga
X _{MCl3}	Fixed	0.67

Table 2 Engineering and chemical variables for the oligomerisation process.

DoE approach to oligomerisation

The variables that could affect the outcome of the reaction could be divided into three categories: engineering, chemical, and directly related to the selected ionic liquid (see Table 2). In order to limit the size of the experimental design matrix, most of these parameters were fixed on one level (in other words, were not varied).

As can be seen in Table 2, out of the 12 parameters, 8 were fixed, and 4 were chosen as variables. These latter parameters (time, temperature, mol % of catalyst and stirring speed) have been demonstrated (or are expected) to have a strong influence on the process, are quantifiable and easily measurable, and therefore ideal for a DoE approach.

The range of reaction time and stirring speed was chosen based on the preliminary experiments and common sense. The lower temperature limit (-5 °C) is a limit of the cooling unit (taking into account buffering the exothermic reaction effect), while the upper limit (21 °C) is only 8 °C lower than the boiling point of 1-pentene. The lower limit of the catalyst concentration was based on experience from the preliminary experiments. The highest value was limited by the cooling capability: addition of larger amounts resulted in an uncontrolled temperature rise.

There were three responses defined for the process: conversion, amount of C20–C50 oligomers in the product (desired range) and amount of >C50 oligomers in the product (undesired range), all expressed in mass %.

It was expected that a second-order response surface model (RSM) would be most appropriate; for example, increase of conversion with temperature may fit better to the quadratic than the linear model. Therefore, a CCD was chosen (see Fig. 2), with six repetitions of the central point. The overall design involved four factors varied over five levels ($-\alpha$, -1, 0, +1, and $+\alpha$), as shown in Table 3.

	1	01	2 31 2	/-		
		$-\alpha$	-1	0	+1	+α
Time/min	А	0	25	50	75	100
Temperature/°C	В	-5.0	1.5	8.0	14.5	21.0
Catalyst conc./mol %	С	0	0.15	0.30	0.45	0.60
Stirring speed/rpm	D	500	750	1000	1250	1500

Table 3 Actual values for all factors and levels for the four-factor CCD full-size matrix for oligomerisation of 1-pentene using $[C_2mim][Ga_2Cl_7]$.

The value of α for the matrix (see Fig. 2) was computed using Design Expert 7.1 [30]. The full experimental matrix of 30 experiments is presented in Table 4. The order of carrying out the experiments was randomised (see the run order in Table 4). The results of the conducted experiments (responses) and analysis of the experimental error are also given in Table 4.

Each response (e.g., conversion) was modelled as a function of the four factors (A, B, C and D). After assigning the RSM to each response (based on R^2), equations for the response surface were derived. A general equation for a response y, in coded values, is given in eq. 1

$$(y+a)^{b} = \beta + \beta_{A}A + \beta_{B}B + \beta_{C}C + \beta_{D}D + \beta_{AB}AB + \beta_{AC}AC + \beta_{AD}AD +$$
(1)
$$\beta_{BC}BC + \beta_{BD}BD + \beta_{CD}CD + \beta_{A}^{2}A^{2} + \beta_{B}^{2}B^{2} + \beta_{C}^{2}C^{2} + \beta_{D}^{2}D^{2}$$

where *a* and *b* are mathematical transformation constants (used to improve the fit), β is an intercept, β_A relates to strength of influence of the factor A on the response, β_{AB} relates to strength of the A × B interaction, β_A^2 determines the strength of the quadratic effect of the factor A, etc.

The lowest part of Table 4 reports the mean, the standard deviation, the mean standard deviation, and the percentage relative error for the six central points (entries 25-30, Table 4). While the relative error is relatively low for the C20–C50 response (ca. 4%) and acceptable for >C50 response (ca. 10%), it is higher for the conversion response (ca. 16%). Sources of the error common for all three responses may be: hydrolysis of the catalyst (very limited by use of glovebox and dinitrogen atmosphere), and contact issues (a simple stirred-tank reactor is used for contacting biphasic liquid mixtures, with the hydrocarbon phase dramatically changing viscosity during the course of reaction). An additional source of error in the case of conversion might be the high volatility of 1-pentene, which could partially evaporate while processing the mixture after reaction, even before it was weighed. Nevertheless, despite the significant scatter of the results, the models of all responses were statistically valid (vide infra).

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					Factors							
Order		C	Coded values Actual values					Re	Responses/%			
Standard	Run	A	В	С	D	A/min	B/°C	C/mol %	D/rpm	Conversion	C20–C50	>C50
1	2	-1	-1	-1	-1	25	1.5	0.15	750	5.84	3.09	0.99
2	1	1	-1	-1	-1	75	1.5	0.15	750	3.60	2.09	0.68
3	14	-1	1	-1	-1	25	14.5	0.15	750	3.93	2.28	0.79
4	18	1	1	-1	-1	75	14.5	0.15	750	7.49	4.42	0.97
5	25	-1	-1	1	-1	25	1.5	0.45	750	18.48	10.72	2.03
6	23	1	-1	1	-1	75	1.5	0.45	750	44.74	27.29	3.58
7	20	-1	1	1	-1	25	14.5	0.45	750	24.10	15.90	2.65
8	15	1	1	1	-1	75	14.5	0.45	750	73.35	51.34	5.87
9	9	-1	-1	-1	1	25	1.5	0.15	1250	6.20	3.47	0.87
10	26	1	-1	-1	1	75	1.5	0.15	1250	6.12	3.92	1.35
11	22	-1	1	-1	1	25	14.5	0.15	1250	3.97	2.54	0.79
12	30	1	1	-1	1	75	14.5	0.15	1250	13.15	8.94	1.71
13	12	-1	-1	1	1	25	1.5	0.45	1250	14.78	8.42	2.36
14	21	1	-1	1	1	75	1.5	0.45	1250	32.64	20.57	4.24
15	5	-1	1	1	1	25	14.5	0.45	1250	26.15	17.00	2.61
16	29	1	1	1	1	75	14.5	0.45	1250	98.32	75.71	10.82
17	4	-2	0	0	0	0	8	0.3	1000	0.00	0.00	0.00
18	28	2	0	0	0	100	8	0.3	1000	16.41	10.34	2.95
19	27	0	-2	0	0	50	-5	0.3	1000	2.66	1.84	0.37
20	6	0	2	0	0	50	21	0.3	1000	14.79	9.32	1.78
21	16	0	0	-2	0	50	8	0	1000	0.08	0.00	0.00
22	7	0	0	2	0	50	8	0.6	1000	99.31	73.49	12.91
23	17	0	0	0	-2	50	8	0.3	500	9.91	5.75	1.49
24	8	0	0	0	2	50	8	0.3	1500	10.52	6.63	1.16
25	24	0	0	0	0	50	8	0.3	1000	11.49	7.35	1.49
26	11	0	0	0	0	50	8	0.3	1000	18.40	10.49	2.94
27	19	0	0	0	0	50	8	0.3	1000	24.81	14.39	2.23
28	3	0	0	0	0	50	8	0.3	1000	24.43	14.42	2.20
29	10	0	0	0	0	50	8	0.3	1000	37.39	22.81	5.23
30	13	0	0	0	0	50	8	0.3	1000	20.82	13.12	2.50
					mea	n, \overline{Y} , for i	n = 6 (er	ntries 25–30)*	22.89	66.50	12.17
					stan	dard devia	ation*			8.61	6.47	2.79
					mea	n standar	d deviati	on $(\sigma)^*$		3.61	2.72	1.17
relative error, $100\sigma \overline{Y}^{-1}$ /%							15.79	4.09	9.61			

Table 4 Experimental plan for oligomerisation of 1-pentene using $[C_2mim][Ga_2Cl_7]$, along with the results of the experiments (responses) and a statistical analysis of the data.

A = time, B = temperature, C = catalyst concentration, D = stirring rate, C20–C50 = mass percentage of olefins C20 to C50 in the product; >C50 = mass percentage of high-end oligomers in the product; * = value in given units.

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Coefficients of the equations in coded values for each response are given in Table 5. Coded values reveal the relative influence of each factor on the response. After replacing the coded values with the actual values (also listed in Table 5), it is possible to calculate the value of the expected response for the given values of the factors.

	Co	oded values		Actual values				
Response (y)	Conv.	C20-C50	>C50	Conv./%	C20-C50/%	>C50/%		
R^2	0.9185	0.9523	0.9336	0.9185	0.9523	0.9336		
Transformation	$(y + 0.99)^{0.5}$	$(y)^{0.5}$	_	$(y + 0.99)^{0.5}$	$(y)^{0.5}$	_		
β	4.56	3.66	2.18	2.50947	2.53423	2.92116		
А	0.86	0.68	0.62	0.021064	0.03419	-0.027664		
В	0.54	0.45	0.32	-0.068407	-0.013 349	-0.019692		
С	1.94	1.40	1.30	-8.8892	-15.86317	-16.02267		
D	_	_	_	_	_	_		
$A \times B$	0.43	0.28	0.23	2.65×10^{-3}	1.80×10^{-3}	1.44×10^{-3}		
$A \times C$	0.68	0.48	0.52	0.18009	0.13117	0.14		
$A \times D$	_	_	_	_	_	_		
$B \times C$	0.43	0.32	0.26	0.43881	0.33424	0.26833		
$B \times D$	_	_	_	_	_	_		
$C \times D$	_	_	_	_	_	_		
A ²	-0.39	-0.39	_	-6.19×10^{-4}	-5.97×10^{-4}	-5.21×10^{-3}		
B ²	-0.30	-0.33	-0.28	-7.04×10^{-3}	-6.69×10^{-3}	25.9359		
C^2	0.35	0.59	0.63	15.47824	26.91084	5.94×10^{-8}		
D^2	_	-0.26	-0.21	_	3.87×10^{-9}	2.92116		

Table 5 Estimated coefficients β , according to eq. 1, for regression models in the terms of coded and actual values.

A = time, B = temperature, C = catalyst concentration, D = stirring rate.

Conversion

Response surfaces for selected factor values are presented in Fig. 5. According to the generated RSM, conversion depends on the reaction time, temperature, and on the catalyst content, each of them fitting to a second-order model. The influence of the catalyst content is much stronger than the effects of either reaction time (Fig. 5a) or temperature (Fig. 5b). Furthermore, the reaction time affects conversion more than the temperature of reaction (Fig. 5c). There are synergies between each pair of three significant factors, the reaction time—catalyst concentration one being stronger than the others.

Noteworthy, stirring speed—within the examined range of values—has no significant effect on conversion.



Fig. 5 Conversion as a function of the three factors: (a) A = time/min, (b) $B = temperature/^{\circ}C$ and (c) C = catalyst amount/mol %; for a–c, the third (fixed) factor is set on the highest level, which allows presentation of the desired area of high conversion.

Content of the desired C20-C50 fraction

In contrast to the conversion RSM, stirring was found to have a small but statistically significant influence on this model (Fig. 6). Nevertheless, considering calculated error for this response, the influence of the stirring speed may be considered negligible from the practical point of view.

The influences of the reaction time, temperature, and the catalyst ratio on the C20–C50 content are similar to the influence of those factors on conversion (Fig. 7). Again, impact of the catalyst concentration is the strongest compared to the reaction time and temperature (Figs. 7b,c), with a strong synergy between temperature and catalyst concentration (Fig. 7c). The disproportion between the effects of temperature and reaction time is lower here compared to conversion (Fig. 7a).



Fig. 6 Influence of D = stirring on the C20–C50 content, compared to the influence of (a) C = catalyst concentration/mol %, (b) B = temperature/°C.



Fig. 7 Content of the C20–C50 fraction as a function of: (a) A = time/min, (b) $B = temperature/^{\circ}C$ and (c) C = catalyst amount/mol %; the fixed factors are set on the maximum levels, with the exception of stirring, set on 1000 rpm (this setting gives the highest response value).

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Content of the undesired >C50 fraction

High boiling oligomers (>C50) are an undesired by-product, and their presence should be minimised. The content of the >C50 cut is a function of all four factors (see Table 6), and the catalyst concentration still has the strongest positive influence (Fig. 8), with an extremely weak influence of stirring. The influence of the reaction time on this response is more pronounced than the influence of time on conversion and C20–C50 content (Fig. 8a); in other words, prolonged reaction time will likely result in an increased amount of the high boiling products. Moreover, the time–catalyst interaction has a rather high synergistic influence on this response (Fig. 8b), which strongly points towards shortening of the reaction time and increasing the temperature in order to minimise content of the >C50 cut.

Table 6 Results of numerical optimisation and	values of the desirabilit	y function D , o	depending on se	t goals and
their importance. All goals weighted at 1.				

Importance			Parameters				Responses/mass %			D
Conversion	C20-C50	>C50	Time/ min	Temp./ °C	Catalyst/ mol %	Stirring/ rpm	Conversion	C20–C50	>C50	
In range	Maximise, importance 5	In range	56.08	14.50	0.45	1000	61.40	40.18	4.67	0.65
In range	Maximise, importance 5	Minimise, importance 2	50.82	14.50	0.43	1000	51.54	33.81	4.15	0.62
Maximise, importance 3	Maximise, importance 3	Minimise, importance 5	54.85	14.50	0.40	1000	45.34	28.81	3.73	0.61



Fig. 8 Content of >C50 oligomers presented as a function of (a) A = time/min and B = temperature/°C, (b) A = time/min and B = catalyst concentration/mol %.

Optimisation of the process

Although the preliminary conclusions regarding optimum conditions could be drawn based on analysis of the model equations, it is beneficial to carry out numerical and graphical optimisation using Design Expert 7.1 software.

The numerical optimisation may be aimed at defined goals, such as maximisation or minimisation of the chosen responses (e.g., maximum conversion with minimised >C50); also, a range of desired values for selected responses may be chosen. Each goal is given an importance factor (1–5) and weight. These goals are combined into an overall desirability function, **D**, and the software seeks to maximise this function (that is, to find values of the four variables that give values of responses as close to the goal values as possible). Whether the calculation will, for example, gravitate towards minimisation of >C50, or maximisation of the conversion, depends on assigned importance and weights. Examples of the numerical optimisation results are shown in Table 6.

High conversion and high C20–C50 content are preferred and related to each other, whereas >C50 oligomers are undesirable. A maximised C20–C50 content can reach up to 40.18 mass %, with conversion 61.40 mass %. Strong emphasis on minimisation of the >C50 content (to 3.73 mass %) results in conversion decreasing to 45.34 mass %, with only 28 mass % of the desired C20-C50 oligomers. Final choice of the parameters depends on the economic advantage offered by each of the optimisations. Importantly, all outputs are optimal for a stirring rate of 1000 rpm and a temperature of 14.5 °C (maximised), whereas the catalyst concentration (0.40–0.45 mol %) and the reaction time (ca. 53 min) vary depending on the set goals. At these values of stirring and temperature, a graphical optimisation was performed (Fig. 9) by manipulating with the reaction time and the catalyst amount values.



Fig. 9 Graphical optimisation of the oligomerisation of olefins; limiting factors: content of oligomers over C50 on maximum level of 5 mass %, content of C20–C50 oligomers on a minimum level of 35 mass %. Temperature (14.5 °C) and the stirring speed (100 rpm) are fixed.

The graphical optimisation requires assigning lower and/or upper limits to the examined responses. Next, their contour plots are overlaid. The white region on the graph (Fig. 9) represents the best outcome, and in this case its area is limited by only two curves: minimum content of C20–C50 oligomers range (35 mass %), and maximum content of C50 range (5 mass %). This area represents a range of catalyst concentrations and reaction times, where the oligomerisation product would have a satisfactory composition. Again, the choice between the longer time and lower catalyst concentration or vice versa is a matter of economics.

CONCLUSIONS

A chlorogallate(III) ionic liquid, a more stable alternative to chloroaluminate(III) systems, was demonstrated to catalyse oligomerisation of 1-pentene to lubricant base oils. Using the DoE approach, it was demonstrated that products of the desired C20–C50 range could be obtained in a high yield, and the

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product distribution could be statistically analysed. It was possible to create a second-order polynomial model of the three responses: total conversion, content of the desired C20–C50 fraction, and undesired >C50 fraction, as a function of the reaction time, reaction temperature, stirring rate and the catalyst concentration.

It was established that—within the tested range of factors—the concentration of the catalyst had the highest influence on the product distribution, with significant impact of the reaction time and temperature, and minimal influence of stirring rate. A number of synergies between the factors were detected.

Optimisation of the responses allowed prediction of the experimental conditions in such a way that it gave an insight into the nature of the reaction. For example, it was shown that higher temperature increased conversion and aided to suppress production of the very long oligomers, which is in accord with the literature [31]. Furthermore, it was shown that manipulating the catalyst concentration and the time of the reaction allows further optimisation of the olefin distribution.

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