

Cleavage path way and the product distribution pattern during the electrochemical perfluorination of tripropylamine

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Abstract

The electrochemical fluorination (ECF) of tripropylamine (TPA) was carried out in anhydrous hydrogen fluoride medium using a Simons type cell. Under optimum conditions, yield of perfluorinated product was about 51% and the selectivity of perfluorotripropylamine (PFTPA) was about 87%. Even in this process involving the well-known starting material, apart from PFTPA, about nine perfluorinated by-products were also identified. Perfluorinated products obtained were characterized by GC, ¹H and ¹⁹F NMR spectra and were compared with reported values. The perfluorinated products obtained support the fission and formation of C–C and C–N bonds. The nature of the minor products formed also supports the involvement of cyclization and isomerization reactions during electrochemical fluorination. Suitable reaction schemes for the formation of different perfluorinated by-products were suggested based on the identified products obtained from ECF of TPA which clearly supports the free radical mechanistic pathway for this process. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Perfluorotripropylamine (PFTPA) has already found commercial applications as an inert liquid in electronic industries [1] and oxygen solubilising medium in bio-medical applications [2]. PFTPA is produced in fairly large quantities by electrochemical perfluorination (ECPF) of tripropylamine (TPA). However, there are only few reports on optimization, product selectivity and mechanism of the process. Widely different yields between 28 and 60% are reported [3–5]. Partially fluorinated starting materials have also been used [6,7]. Fairly high cell voltages (upto 6.5 V) have also been recommended [7]. Further work to understand some of the issues cited is desirable.

Recently an effort was made to ascertain the pathway of electrochemical fluorination (ECF) by identifying the product distribution including the minor constituents obtained from the ECF of *N,N,N',N'*-tetramethylethylenediamine and 2-fluoropyridine [8,9]. A free radical pathway involving highly reactive surface bound high valent nickel fluoride has been suggested [9,10] by us and other workers [11–13]. In this work, an attempt is made to study the yield, product selectivity and mechanistic pathway of ECF of TPA.

2. Experimental details

2.1. Electrochemical cell

A double walled 200 ml capacity stainless steel electrolysis cell with a pack of alternate nickel anodes and cathodes was employed in the present study (effective anode area = 3.0 dm²). Temperature of the cell and the condenser was maintained at 0 and –30 °C, respectively, using cryostats. Volatile products were collected in a PTFE-FEP traps kept at –78 °C using a dry ice–ethanol mixture at the outlet of the cell. Liquid products from the cell were drained through a ball valve at the bottom of the cell. A 1 l capacity (active anode area = 14 dm²) ECF cell was used in Exp. no. 7.

2.2. Electrochemical fluorination of tripropylamine

Pre-electrolysis was done at the start of each experiment in order to dry anhydrous hydrogen fluoride (AHF) and activate electrode surfaces. Pre-electrolysis was carried out for about 36–48 h till the initial current of 4 A reduces to 0.2 A. Cell voltage was maintained between 5.0–5.5 V during this period. A required quantity of TPA and AHF mixture was prepared separately before each addition of amine.

ECF was carried out under galvanostatic condition at various current densities from 0.67 to 2.3 A dm^{–2}. TPA

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concentration of 6% (w/v) was taken initially and the electrolysis was carried out in a Pre-electrolysed AHF medium till the concentration of TPA reaches 1.5%. This was done by passing the theoretical current of electricity required to fluorinate 4.5% (9.0 g) of TPA. Required concentrations of TPA and AHF were maintained periodically. After passing pre-determined electricity (100 or 105% of electricity as the case may be) the electrolysis was stopped. Crude perfluorinated products obtained were neutralised with a dilute solution of sodium bicarbonate and washed thoroughly with distilled water and finally anhydrous sodium sulphate was added to remove moisture.

The AHF phase containing soluble partially fluorinated amines was diluted with ice cold water and the partial fluorinated amines were separated out as a heavy liquid. They were neutralised, washed and dried.

2.3. Separation and identification of perfluorinated products

The mixture of perfluorinated products obtained from the cell was separated by fractional distillation. About 64.8 g of perfluorinated products obtained from ECF (Exp. no. 1) of TPA was taken for fractional distillation. Distillation gave the following three fractions.

2.3.1. Fraction-I (bp < 110 °C)

First drop was collected at 55 °C and there was steady rise of temperature to 110 °C. About 3.61 g of products were collected in this fraction.

2.3.2. Fraction-II (bp 122–127 °C)

About 48.43 g of perfluorinated products were collected in this fraction.

2.3.3. Residue (>127 °C)

The residue contains about 12.73 g of perfluorinated products.

Gas chromatograms were recorded on a Perkin-Elmer gas chromatograph (10% Apiezon on chromosorb WAW, 100–120 mesh, column length 2.5 m and 2 mm i.d.). Temperature

of the injector, column and the detector (FID) were held at 160, 100 and 200 °C, respectively. Helium was used as carrier gas.

¹⁹F and ¹H nuclear magnetic resonance spectra were recorded for neat liquids without solvent using CD₃CN film in a Bruker WP 80SY spectrometer (80.1 MHz for proton and 75.4 MHz for ¹⁹F). CCl₃F and TMS were used as internal references. The resonance at high field of the reference was designated as negative.

3. Results and discussion

3.1. Optimization studies

Typical results obtained during the ECF of TPA under different experimental conditions are presented in Table 1. In these experiments, the cell voltage was generally maintained around 5.0 V and even under very low reactant concentrations, the cell voltage was not allowed to exceed 5.5 V. This was found to be a critical factor for maintaining the activity of nickel fluoride anodic film and also for controlling the activity of active fluorine and thus to minimize decomposition products.

When the theoretical quantity of electric current was passed at 1.0 A dm⁻², substantial quantities of partially fluorinated products were found to remain in the HF phase (Table 1, Exp. no. 1). This amount could be reduced and simultaneously perfluorinated product could be increased by increasing the total charge passed to 105% (Table 1, Exp. no. 2). At lower current density even with 105% of theoretical charge the partially fluorinated compound in HF phase increased further (Table 1, Exp. no. 3). At the optimum current density of 1.6 A dm⁻², maximum yield of perfluorinated product with very little quantity of partially fluorinated product in the HF phase could be achieved (Table 1, Exp. no. 4). Further increase in current density, however, leads to C–C and C–N bond cleavage and hence lower yields although partially fluorinated products in the HF phase are absent (Table 1, Exp. no. 5). Initial concentration of TPA was increased from 6 to 9% to see if further improvement

Table 1
Effect of experimental parameters on the yield of perfluorinated products

Exp. no.	Concentration of TPA (%)	Total amount of TPA added (g)	Current density (A dm ⁻²)	Amount of PFP obtained (g)	Amount of part. fluoroamine obtained (g)	Yield of PFP obtained (%) ^a
1	6	54.6	1.0	69.2	18.5	35
2	6	54.0	1.0	87.3	12.7	45
3	6	50.6	0.67	56.6	16.5	31
4	6	50.0	1.67	92.4	Nil	51
5	6	50.5	2.3	73.8	Nil	41
6	9	47.5	1.67	86.6	Nil	50
7	6	144.5	1.0	230.3	Black colour	45

Note: theoretical charge (100%) was passed for Exp. no. 1 and for other experiments five percent excess of charge (i.e. 105%) was passed. Cell voltage = 5.0–5.5 V. TPA: tripropylamine; PFP: perfluorinated products; part.: partially.

^a Purified perfluorinated amines only.

in the overall product yield could be achieved as shown in Exp. no. 6 in Table 1. This procedure did not lead to any improvement in overall product yield.

The optimisation study in the 200 ml capacity cell thus suggests that under optimum experimental conditions a total product yield of 51% can be easily achieved. These experimental conditions also ensure minimum level of build up of partially fluorinated organic compounds in the HF phase ensuring prolonged continuous operation of the electrochemical reactor.


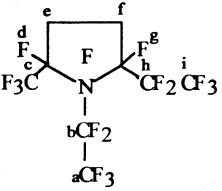
One experiment was also performed in the 1 l reactor to obtain sufficient quantity of perfluorinated products for further studies and also to assess the reproducibility. Under similar conditions around 45% product yield could be achieved (compare Exps. no. 2 and 7 in Table 1).

3.2. Product distribution

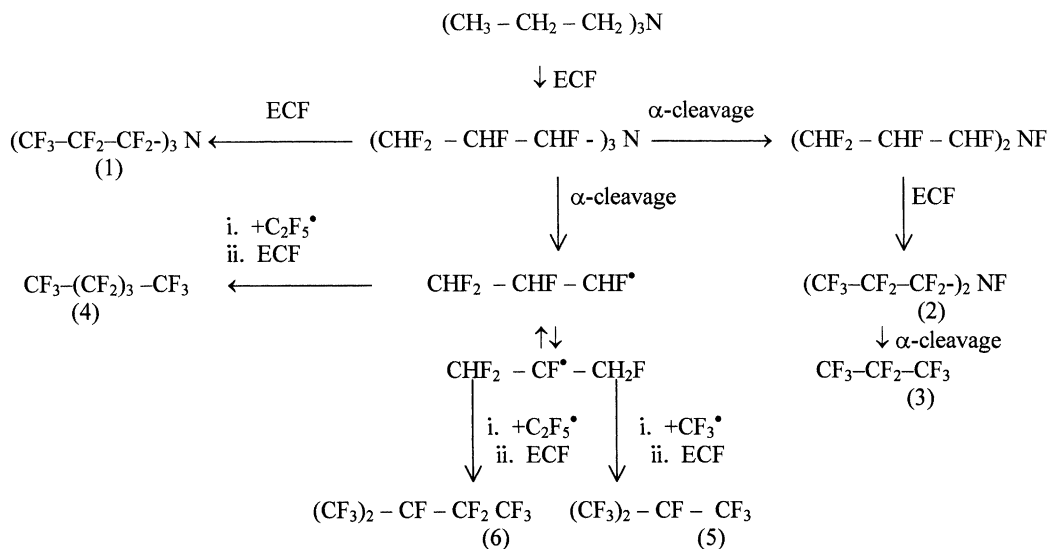
Under optimum conditions ECF of TPA was also found to be highly selective. An overall selectivity of 87% was achieved (Table 2, Product 1). The product selectivity indeed seems to depend very much on the operating conditions as reported by different workers [3–7]. Such wide differences are probably due to the complexity of the procedures involved.

In the crude product obtained under the present experimental conditions, proton NMR studies indicated only trace levels of partially fluorinated compounds which could not be quantitatively analysed. However, the presence of CHF₂ and CHF groups was confirmed by NMR studies. It, thus, appears that under the mild experimental conditions suggested here

Table 2
¹⁹F NMR data of products obtained from ECF of tripropylamine and their selectivity

Product no.	Structure of the products obtained	Chemical shifts (δ ; ppm vs. CFCl ₃) observed	Angular momentum (J ; Hz)	Selectivity (%)	Reference
1	$(\overset{a}{\text{CF}_3}-\overset{b}{\text{CF}_2}-\overset{c}{\text{CF}_2})_3\text{N}$	CF ₃ ^a = -81.5 br, s CF ₂ ^b = -121.0 sept. CF ₂ ^c = -83.8 br, m	³ J(F ^a -F ^b) = 9.8 Hz	87.0	
2	$(\overset{a}{\text{CF}_3}-\overset{b}{\text{CF}_2}-\overset{c}{\text{CF}_2})_2\text{N}-\overset{d}{\text{F}}$	CF ₃ ^a = -82.2 CF ₂ ^b = -126.7 d CF ₂ ^c = -106.2 d sept. NF = -91.0 m	³ J(F ^{c-d}) = 23.1 Hz ⁴ J(F ^{b-d}) = 19.9 Hz ⁴ J(F ^{a-c}) = 4.2 Hz	1.39	[14]
3	CF ₃ -CF ₂ -CF ₃	CF ₃ = -84.0 t CF ₂ = -130.5 br, s	³ J(F-F) = 8.6 Hz		[15]
4	$\overset{a}{\text{CF}_3}-\overset{b}{\text{CF}_2}-\overset{c}{\text{CF}_2}-\overset{d}{\text{CF}_2}-\overset{e}{\text{CF}_3}$	CF ₃ ^{a,c} = -81.8 m CF ₂ ^{b,d} = -126.6 m CF ₂ ^c = -123.3 m		1.67	[16]
5	$\begin{array}{c} \text{F} \\ \\ \text{CF}_3-\text{C}-\text{CF}_3 \\ \\ \text{CF}_3 \end{array}$	CF ₃ = -71.1 d CF = -180 m	³ J(F-F) = 8.6 Hz		[17]
6	$(\overset{a}{\text{CF}_3})_2\overset{b}{\text{CF}}-\overset{c}{\text{CF}_2}-\overset{d}{\text{CF}_3}$	CF ₃ ^a = -72.7 d, t, q CF ^b = -186.8 m CF ₂ ^c = -116.1 sept. CF ₃ ^d = -82.3 d, t	⁴ J(F ^{a-c}) = 9 Hz	0.56	[9,18]
7	$(\overset{a}{\text{CF}_3}-\overset{b}{\text{CF}_2}-\overset{c}{\text{CF}_2})_2\text{N}-\overset{d}{\text{CF}_3}$	CF ₃ ^a = -81.9 CF ₂ ^b = -124.7 sept. CF ₂ ^c = -88.5 br, m CF ₃ ^d = -50.7 m CF ₃ = -56.5 s	³ J(F ^{a-b}) = 9.6 Hz	0.84	[19]
8	(CF ₃) ₃ N	CF ₃ N = -53.2 sept. CF ₂ N = -91.2 m/q CF ₃ ^a = -84.8 m CF ₂ = -133.4 s	³ J(F ^{a-b}) = 15.2 Hz ⁵ J(F ^{a-c}) = 7.6 Hz		[8]
9	$(\overset{a}{\text{CF}_3}-\overset{b}{\text{CF}_2})_2\text{N}-\overset{c}{\text{CF}_3}$	CF ₃ N = -53.2 sept. CF ₂ N = -91.2 m/q CF ₃ ^a = -84.8 m CF ₂ = -133.4 s	³ J(F ^{a-b}) = 15.2 Hz ⁵ J(F ^{a-c}) = 7.6 Hz		[20]
10		CF ₃ ^a = -85.1 d CF ₂ ^b = -88.9 br CF ₃ ^c = -75.0 d, m CF ^d = -156.5 d, br CF ₂ ^e = -124 br CF ₂ ^f = -126 d, br CF ^g = -162 d, br CF ₂ ^h = -124 br CF ₃ ⁱ = -80 d, t	⁴ J(F ^{g-i}) = 16.6 Hz ³ J(F ^{h,i}) = 8.7 Hz ⁵ J(F ^{a-d}) = 7.9 Hz	7.48	[21]
11		CF ₃ ^a = -85.1 d CF ₂ ^b = -88.9 br CF ₃ ^c = -75.0 d, m CF ^d = -156.5 d, br CF ₂ ^e = -124 br CF ₂ ^f = -126 d, br CF ^g = -162 d, br CF ₂ ^h = -124 br CF ₃ ⁱ = -80 d, t	⁴ J(F ^{g-i}) = 16.6 Hz ³ J(F ^{h,i}) = 8.7 Hz ⁵ J(F ^{a-d}) = 7.9 Hz	7.48	

Note: s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sept., septet; br, broad; m, multiplet.

Scheme 1. Reaction path for the formation of products from C_α-N bond cleavage.

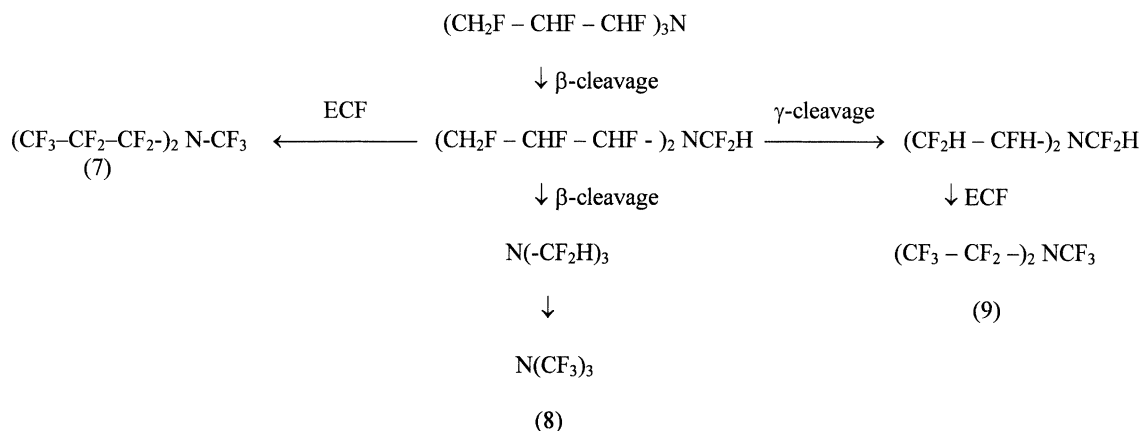
formation of partially fluorinated compounds that are miscible with perfluorinated products is indeed small. This factor is quite important since removal of partially fluorinated compounds from the perfluorinated product is extremely important [2] and quite sophisticated purification procedures are necessary [11–13].

Although, the selectivity of PFTPA was quite high it was still possible to identify at least 10 other perfluorinated products by careful analysis of the different distilled fractions. As suggested earlier during the ECPF of *N,N,N',N'*-tetramethylethylenediamine [8] and 2-fluoropyridine [9], such a wide variety of side product formation is probably due to bond cleavage and free radical re-arrangements of partially fluorinated intermediates. Schemes 1–3 present the cleavage pattern and the decomposition products identified are marked with specific numbers. The NMR data of such identified products are summarised in Table 2 along with literature references wherever available.

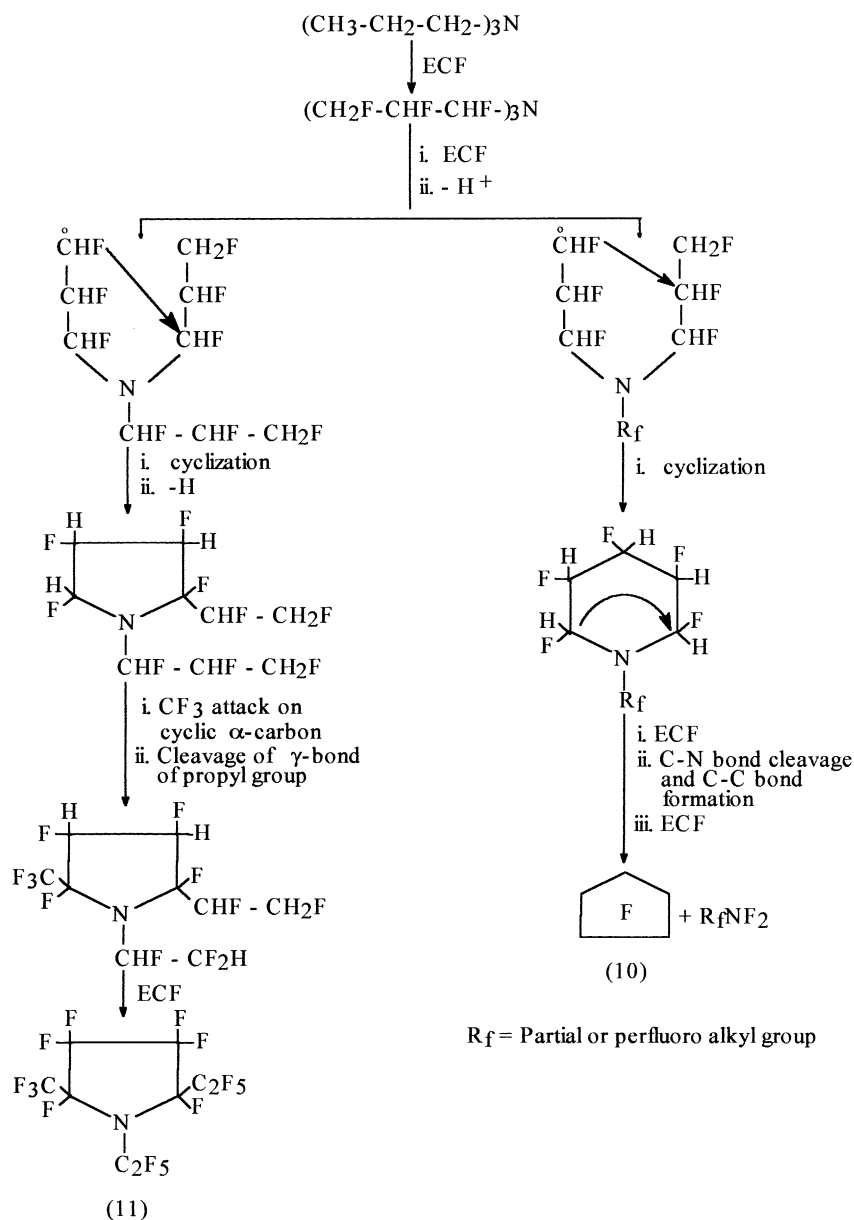
The distribution of cleavage products clearly indicate that all the three bond cleavages namely N-C_α, C_α-C_β and C_β-C_γ occur during ECF process. Product 2, for e.g. is due to the cleavage of N-C_α bond (Scheme 1). Products 7 and 8 are formed due to the cleavage of C_α-C_β bond. Product 9 is obtained due to C_α-C_β and C_β-C_γ bond cleavages (Scheme 2).

During cleavage processes, perfluoromethyl, ethyl and propyl radicals are also generated. These radicals can combine among themselves to form a number of perfluorocarbons. The reaction pathways leading to the identified perfluorocarbons are presented in reaction Scheme 1. Direct combination of the radicals would lead to compounds 3 and 4. The transformation of primary perfluoropropyl radical into a more stable secondary radical followed by further reactions would lead to compounds 5 and 6 (Scheme 1).

Quite interestingly, cyclisation products are also formed during the ECF of TPA. Substituted pyrrolidine compound



Scheme 2. Reaction scheme for the formation of products from β- and γ-bond cleavages.



Scheme 3. Schematic pathway for the formation of cyclic products from the ECF of tripropylamine.

11 is indeed found to be the most important by-product accounting for 7.5% of the yield. This is, indeed, an isomer of PFTPA and the possible reaction pathway is indicated in Scheme 3. Similar yield of a perfluoropyrrolidine derivative with *N*-perfluoropropyl group has been indicated in an earlier work [7]. However, our NMR data fits well with the structure indicated in Table 2. Perfluorocyclopentane is another interesting compound obtained in substantially lower yield. This compound may be found through cyclisation followed by C–N bond cleavage as indicated in Scheme 3.

Table 2 contains some compounds like PFTPA which possess fairly low boiling point. However, due to their strong interaction with other perfluorinated products these compounds still exhibit their presence in the relatively high

boiling fractions. Most of the by-products from 2 to 10 were present in fraction-I. product 11 was identified in fraction-II along with PFTPA. Some of the low boiling products like 3–6 and 8–10 were collected below 70 °C. However, some of them remained trapped in the fluid up to 110 °C.

Since the present work only collected and analysed the perfluorinated liquid fraction obtained through the bottom discharge of the electrochemical reactor, the by-products identified here should not be considered as exhaustive or comprehensive. However, these products themselves provide substantial evidence for the free radical pathway of overall ECF reaction [8–10]. Hence, by proper control of the free radical generation at the electrode surface and by optimising the reactant concentration in the electrolyte,

substantial improvement in the yield and selectivity of perfluorinated products can be achieved.

4. Conclusions

ECF of TPA in AHF gave perfluorinated amines as well as partially fluorinated amines. Passing 5% excess of theoretical electricity increases the yield of perfluorinated amine. Higher yield of perfluorinated products (up to 51%) could be obtained at a current density of 1.67 A dm^{-2} and by passing 105% of electricity. Under such conditions partially fluorinated products are almost absent while diluting the AHF phase. Reproducible results are also obtained from a higher capacity ECF cell.

The products were characterised by GC, ^{19}F and ^1H NMR spectra. Selectivity of PFTPA was about 87%. Ten other side products were isolated, which indicated the cleavage of C–C, C–N bonds and formation of C–C bonds, cyclisation and isomerisation reactions. These observations lend further support to the view that the ECPF process occurs mainly through the free radical pathway through a high valent nickel fluoride [8–10]. NMR spectral studies also indicated the presence of traces of partially fluorinated products in the perfluorinated compounds. Further experiments are in progress for the removal of partially fluorinated compounds in the perfluorinated fraction preferably through further optimisation and control of the ECPF process itself.

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