

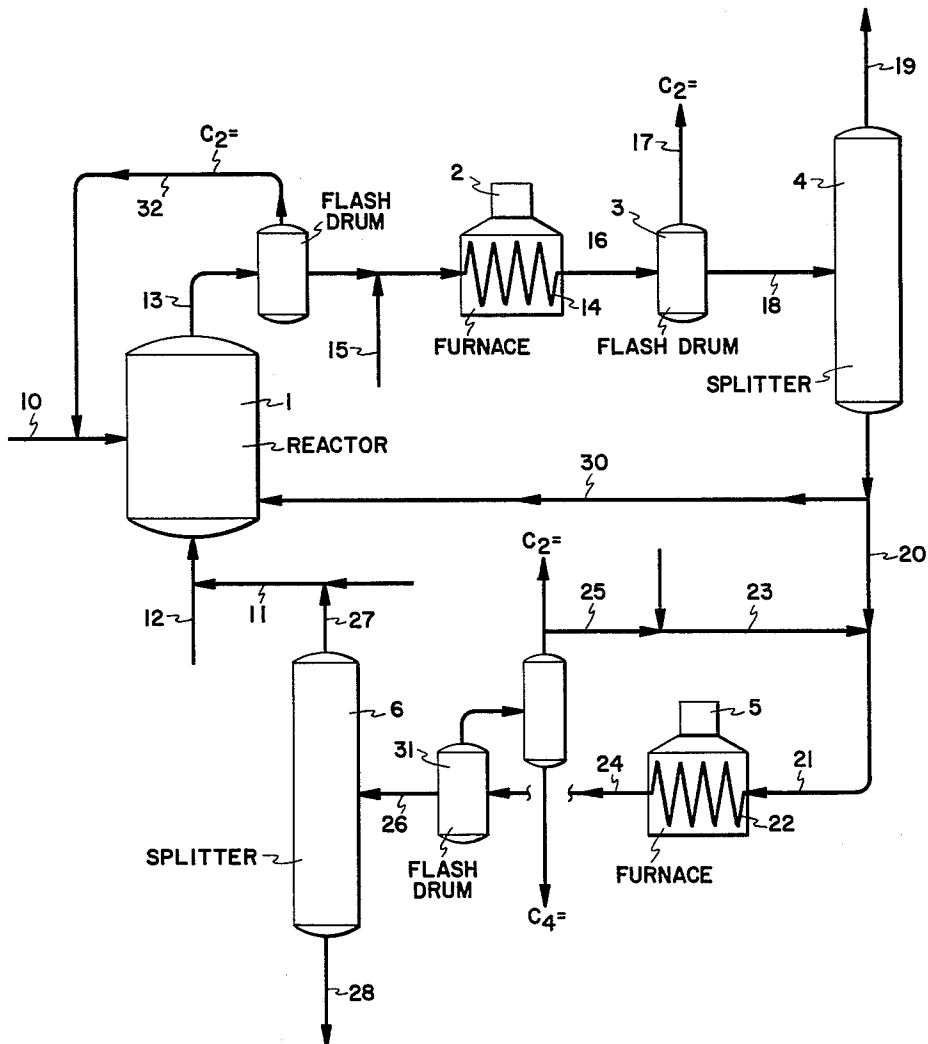
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PREPARATION OF OLEFINS

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3,227,773

## PREPARATION OF OLEFINS

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This application is a continuation-in-part of application Serial No. 835,084, filed August 20, 1959 and now abandoned.

This invention relates to the preparation of  $C_4$  through  $C_{20+}$  normal olefins. More particularly, this invention relates to an improvement over a prior art process for the synthesis of straight chain alpha olefins, said prior art process comprising the steps of: (1) adding or growing ethylene onto low molecular weight aluminum trialkyls to produce higher molecular weight aluminum trialkyls, (2) reacting said growth higher aluminum trialkyls with low molecular weight olefins to obtain a displacement of the higher molecular weight alkyl groups by said lower olefins thus forming higher olefins and lower molecular weight aluminum trialkyls corresponding to the displacing olefins, and (3) separating the displaced higher molecular weight olefins as product from the lower molecular weight aluminum alkyls formed in the displacement reaction, which lower alkyls are recycled to the process.

Still more particularly, this invention relates to the use of two displacement reactions, first employing an olefin having at least one more carbon atom than the individual alkyl groups in the starting trialkyl aluminum and then with ethylene or propylene in a manner which avoids or minimizes the formation of branchiness in the olefin product as well as loss of  $C_2$  or  $C_3$  alkyl aluminum reactant. For ease of description, the number of carbon atoms described in connection with the alkyl aluminum compounds, (e.g.  $C_2$ ) refers to the number in each alkyl group.

Some prior art processes have been limited generally to the production of  $C_8$ – $C_{10}$  olefins, since no practical methods were known for completely separating olefins boiling close to  $C_{10}$ – $C_{14}$  olefins from the  $C_2$  or  $C_3$  alkyl aluminum remaining after the displacement reaction. Thus, the  $C_{12}$  and higher olefins could not be economically distilled overhead from the liquid alkyl aluminum due to the relatively low decomposition temperature of said alkyl aluminum and/or the closely similar boiling ranges of the lower alkyl aluminum and these higher olefins. Thus, according to the same prior art processes, it was considered necessary to closely regulate the growth conditions so as to obtain a minimum amount of  $C_{12}$  and higher olefins. Additionally, those higher olefins which were formed required removal by purging, which involved the loss of an important amount of commingled, valuable alkyl aluminum compounds. Further, in order to keep these alkyl aluminum purge losses to a minimum, the  $C_{12}$  and higher olefin content of the recycle aluminum alkyl stream was often built up to fairly high levels, which also deleteriously affected the process due to the cost of circulating large amounts of this material.

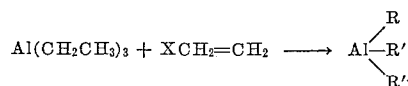
The necessity for a purge stream is entirely eliminated in the present process. This is extremely important in that although in the prior art processes the olefins mixed with the aluminum alkyls in the purge stream can be recovered by hydrolysis, the much more valuable aluminum trialkyls were destroyed in the process. By the present process essentially complete recovery and recycle of alkyl aluminum is obtained, thereby greatly reducing the total cost of the product olefins produced. This is true regardless of whether a full range of olefins is desired or whether, as in prior art processes, production of  $C_8$ – $C_{10}$

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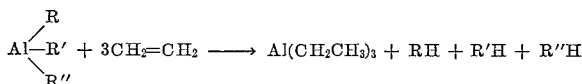
olefins is preferred. In any event growth conditions may now be controlled to obtain the most economic product distribution desired rather than unnecessarily recycling higher alkyl aluminum as was formerly required.

The prior art discloses the basic chemical reactions involved in the present process. They are typified by the following equations:

(1) Growth



(2) Displacement



wherein R, R' and R'' attached to the aluminum atom represent normal alkyl radicals of the same or different molecular weight. RH, R'H and R''H represent normal olefins corresponding to the alkyl radicals referred to above.

In the growth reaction, triethyl aluminum or tripropyl aluminum is reacted with ethylene at a temperature between 200–500° F. and an ethylene partial pressure of 350 to 7500 p.s.i.g. for 0.5 minute to an hour or more. Ethylene radicals are thereby disposed in between the aluminum to carbon bonds in the triethyl aluminum, enlarging the size of the alkyl radicals on the initial trialkyl aluminum by carbon number multiples of two until a trialkyl aluminum product averaging  $C_6$ – $C_{16}$  carbon atoms per alkyl is formed. Starting with triethyl aluminum the growth product will contain even numbered alkyl groups whereas with tripropyl aluminum the growth product will contain odd numbered alkyl groups. With regard to the growth product R, R' and R'' referred to above may in some instances be the same; for example, trihexyl aluminum, tripentyl aluminum, trioctyl aluminum, trinonyl aluminum, tridodecyl aluminum, etc. However, in most instances the alkyl groups of the trialkyl aluminum growth product will be different. As examples, the growth product may contain a trialkyl aluminum compound such as ethylhexyloctyl aluminum, dibutyloctyl aluminum, octyldodecylhexadecyl aluminum, as well as mixed odd numbered trialkyl aluminum compounds when tripropyl aluminum is employed. Occasionally, alkyl aluminum hydrides occur during growth. Insofar as the growth product is concerned, the lowest boiling trialkyl aluminum is triethyl aluminum which boils close to normal  $C_{12}$  alpha olefin under pressures normally desired for fractionation. Tripropyl aluminum boils close to the  $C_{14}$  olefin and tributyl aluminum within the range of  $C_{16}$ – $C_{18}$  olefins. In the displacement reaction, the growth product is reacted with a low molecular weight olefin in predominant amounts at a reasonably high temperature in the order of 400–700° F. and at a pressure of from 0.2–20 atmospheres or the like, preferably for a short period of time, e.g. 0.05 to 10 seconds, thereby generating olefins corresponding to the alkyl groups in the alkyl aluminum growth product and low molecular weight alkyl aluminum compounds.

In order to design an economic commercial olefin plant of this type, it is necessary to have available triethyl aluminum or other low alkyl aluminum such as tripropyl aluminum for the growth reaction, at a reasonable cost. It is therefore considered essential that the triethyl or tripropyl aluminum growth reactant be recovered in relatively pure form for recycle to the growth reactor as alkyl growth reactant.

It is one object of this invention to provide the art with a novel continuous process for producing olefins over the broad spectrum of  $C_4$ – $C_{20+}$  which have little or no branch-

iness in the molecule. It is a further object of this invention to provide the art with a process for the manufacture of the aforesaid straight chain olefins with a maximum of triethyl or tripropyl aluminum recovery in a sufficiently pure state for recycle to the growth reactor. These objects and others which will become apparent are effected by resort to the following described process with specific reference to the appended drawing, schematically illustrating the process. In the exemplary process described, triethyl aluminum is employed as growth reactant whereas this invention also envisions the use of tripropyl aluminum as growth reactant, in which case propylene will be employed in the second displacement zone.

In the drawing, growth reaction zone 1 may be any simple reactor capable of withstanding the necessary pressures and temperatures noted previously. Preferably, however, this reactor will comprise a tubular serpentine-like coil of from 50 to 300 feet in overall length. Since the growth reaction is exothermic and it is necessary to remove heat, heat exchange means must be employed in order to control temperature. While many heat exchange techniques are available, it is preferred to use a tube within a tube. The internal tube of, for example, a diameter of  $\frac{1}{2}$ "-10", preferably under 6", comprises the reactor wherein triethyl is reacted with ethylene. The outer tube which completely encases the inner tube but which otherwise is not connected thereto will contain the circulating coolant. The outer tube should, of course, have an internal diameter substantially greater than the outside diameter of the reactor tube, e.g. 2-4" greater. The coolant should preferably be a medium weight oil. It is advisable not to employ water as a coolant since water hydrolyzes aluminum alkyls quite readily, oftentimes with explosive results. The preferred reactor therefore will in effect be a tube within a tube, the internal tube containing the reactants and the external tube containing the coolant. If desired, fins may be attached to the external wall of the internal tube to increase heat exchange efficiencies. Alternatively, the tubes may be immersed in a cooling medium. Ethylene, preferably in relatively pure state, is introduced into the reaction zone via line 10 with makeup triethyl aluminum via line 12. Triethyl aluminum in line 11 is recycled from a later stage in the process and line 12 is provided to permit adding small amounts of triethyl aluminum makeup. If desired there may be provided multipoint injection of the ethylene and/or triethyl aluminum; however, this is not considered necessary. After the growth reaction is completed within the specified time the growth reaction product containing some unreacted triethyl aluminum and ethylene as well as trialkyl aluminum containing alkyl groups of from 4 to 20+ carbon atoms is removed via line 13 and passed through a tubular coil 14 within furnace 2 wherein the first displacement is effected. Preferably ethylene is flashed off prior to the displacement step by conventional means and recycled to the growth reaction stage via line 32 as ethylene feed. In this displacement reactor substantial amounts of butylene are introduced via line 15 into the growth reaction product stream 13 prior to the first displacement reaction. The first displacement reaction in displacement tube 14 is carried out under the general conditions indicated previously, i.e. preferably 0.05-10 seconds, 400-700° F., pressures of 0.2 to 15 atmospheres. With regard to both displacement reactions, longer residence times, i.e. up to 5 hours, may be employed at temperatures of 60-400° F., but are not preferred due to the tendency of the reactants to undergo undesirable side reactions. It should be recognized that there is no upper pressure limit to this reaction. However, as the pressure level is increased, a growth reaction (reaction 1) tends to take place to a greater extent, thus decreasing the effectiveness of the desired displacement reaction (reaction 2).

As the displacing olefin for the first displacement there should be employed any olefin having at least one more carbon atom than the alkyl groups in the trialkyl alumi-

num growth reactant. Assuming  $n$  represents the number of carbon atoms per alkyl group in the alkyl aluminum growth reactant, the first stage displacement reaction shall preferably employ a  $C_{n+1}$  to  $C_{n+4}$  olefin and more preferably a  $C_{n+2}$  olefin. In this example triethyl aluminum is the growth reactant and butylene is the preferred  $C_{n+2}$  displacement reactant. By converting the growth product to a tri  $C_{n+2}$  alkyl aluminum,  $C_{12}$ - $C_{14}$  and lighter olefins may be separated by economic fractionation. Using  $C_{n+4}$  olefin permits the separation of  $C_{16}$  and lighter olefins; however, it is undesirable to employ an olefin over  $C_{n+4}$  due to the unfavorable economics and difficulty of separation involved.

Referring again to this example, the butylene displaced stream 16 will now contain principally tributyl aluminum and  $C_2$ - $C_{20+}$  normal alpha olefins. Preferably this tributyl aluminum containing stream is passed to flash drum 3 which can be maintained at 20 to 50 p.s.i.g. and 100 to 200° F., whereby generated ethylene is flashed overhead via line 17. Ethylene from this flash drum may be recycled downstream to the second displacement reaction zone as will be described, or part of it may be used as feed to the growth reactor.

The deethylenized tributyl aluminum-olefin containing stream is then passed via line 18 into the tributyl aluminum splitter tower 4 wherein a separation of the  $C_4$ - $C_{14}$  olefins from the tributyl aluminum plus  $C_{16+}$  olefins is carried out. In order to avoid decomposition of the tributyl aluminum and side reactions such as back displacement and isomerization, it is preferable to maintain the bottoms temperature within this tower below about 275° F. and accordingly reduced pressures in the order of  $\frac{1}{2}$  to 10 mm. Hg are required. Under these fractionating conditions a  $C_4$ - $C_{14}$  normal alpha olefin fraction is recovered via line 19 as olefin product and tributyl aluminum plus  $C_{16+}$  olefins are recovered via line 20 for further processing. Thus the first stage alkyl aluminum displacement product is separated from lower boiling olefins up to  $C_{14}$  olefin. The  $C_4$ - $C_{14}$  olefins recovered via line 19 are suitable for the manufacture of straight chain sulfated detergents and have various other known uses. The bottoms from tower 4, i.e. tributyl aluminum and/or other low trialkyl aluminum, e.g. trihexyl aluminum, along with the higher boiling olefins are recovered and the majority of this stream 75-95 wt. percent specifically 85%, is recycled directly to the growth reactor via line 30. This recycle via line 30 is not necessary and in some cases it is desirable, in order to avoid complicating side reaction, to pass the entire bottoms stream from tower 4 onto the second displacement tubes 22 without recycle. The mixed tributyl aluminum-olefin stream which has not been recycled is passed through line 21 with fresh ethylene as well as recycle ethylene from line 17 via line 23 into the displacement reactor tubes. In tubes 22 wherein ethylene will be displacing the butyl groups of the tributyl aluminum, slightly higher pressures may be employed, e.g.  $\frac{1}{2}$  to 20 atmospheres and essentially the same temperature and residence time may be utilized as in the prior displacement reaction. Thus, in a second stage displacement zone the alkyl groups of the first stage alkyl aluminum displacement product are displaced by an olefin having at least one and preferably at least 2 carbon atoms less than said alkyl groups in said first stage alkyl aluminum displacement product. There is then obtained a second stage alkyl aluminum displacement product which can be separated from the remaining olefins and recycled as described hereinafter. In this specific example the product from the second displacement reaction which is removed via line 24 will contain ethylene, butylene, triethyl aluminum and  $C_{16+}$  olefins. The ethylene and butylene may be flashed overhead via a conventional flash drum 31 and after separation of the butylenes, ethylene may be recycled via line 25 back to the second displacement reaction zone. The recovered butylene may be recycled into line 15 for the first displacement reaction. The remain-

ing triethyl aluminum and  $C_{16+}$  olefin are passed via line 26 to the triethyl aluminum splitter tower 6 wherein triethyl aluminum is taken overhead via line 27 and recycled to the growth reaction zone via line 11. Normal alpha olefins having little or no branchiness are recovered via line 28. The temperatures within splitter tower 6 must be maintained sufficiently low to avoid a back displacement, i.e. displacement of the ethyl radicals in the triethyl aluminum by the higher molecular weight olefins, and also isomerization of the alpha normal olefins. Preferably, the temperature within the splitter tower should not exceed 225–275° F. Maximum pressures, of course, should be adjusted to coincide with the maximum temperatures desired in the tower, e.g. 0.5 to 50 mm. Hg, preferably 1–10 mm. Hg.

For a more specific illustration of the complete process, reference may be had to the following table which described all conditions, both generic and specific, necessary for one skilled in the art to practice the aforescribed invention.

Table

Apparatus	Broad	Specific
Growth Reactor 1:		
( $C_2$ Pressure p.s.i.g.)	350–7,500	2,000
(Temp., ° F.)	200–500	320
(Residence, Min.)	0.5–600	12
Line (10) $C_2^-$ (moles)	(1)	1,500
Line (32) $C_2^-$ (moles)		350
Line (11) $Al(Et)_3$ (moles)		97
Line (12) $Al(Et)_3$ (moles)		3
Line (13) $Al(R)_3$ R=Poisson Dist. Average Carbon No.	0–5	12
Displacement Reaction Tube (14):		
(Pressure p.s.i.a.)	3–225	75
(Temp., ° F.)	400–700	570
(Time, Sec.)	0.05–10	0.8
Line (15) $C_4^-$ (Moles)	500–20,000	6,000
Flash Drum (3):		
(Pressure p.s.i.g.)	20–50	30
(Temp., ° F.)	100–200	150
Splitter (4):		
(Temp., ° F.)	200–275	240
(mm. Hg)	$\frac{1}{2}$ –10	1
Line (19) $C_4^-$ – $C_{14}^-$ (moles)	39–270	227.1
Line (21) $Al(C_4)_3$ (moles)	95–100	98.5
Line (23) $C_2^-$ (moles)	300–15,000	3,000
Displacement Reaction Tube (22):		
(Pressure p.s.i.a.)	7–300	125
(Temp., ° F.)	400–700	570
(Time, Secs.)	0.05–10	0.8
Line (26) $Al(Et)_3$ (moles)	95–100	97.5
Splitter (6):		
(Pressure mm. Hg)	$\frac{1}{2}$ –50	3
(Temp., ° F.)	175–275	200
Line (27) $Al(Et)_3$ (moles)	90–100	97
Line (28) $C_{16}^-$ (moles)	10–261	70.8
Line (30) bottoms (wt. percent)	75–95	85

<sup>1</sup> Dependent on mol wt. desired.

What is claimed is:

1. A process for the preparation of olefins which comprises reacting triethyl aluminum with ethylene under ele-

vated temperatures and pressures whereby a higher molecular weight trialkyl aluminum growth product is obtained, reacting said higher molecular weight trialkyl aluminum growth product with butylene at elevated temperatures and pressures to cause a displacement reaction thereby forming a first displacement reaction product mixture which comprises tributyl aluminum and olefins corresponding to the alkyl groups in said higher molecular weight trialkyl aluminum growth products, separating from said displacement reaction product mixture olefins boiling below about the boiling point of tributyl aluminum, reacting the remaining tributyl aluminum and olefins boiling within the range of, and higher than the boiling point of tributyl aluminum with ethylene to form triethyl aluminum and olefins boiling substantially higher than triethyl aluminum, separating said triethyl aluminum from said higher olefins and reacting said separated triethyl aluminum with additional ethylene.

2. A process in accordance with claim 1 wherein said growth reaction is carried out at a temperature of 200–500° F. and a pressure of 350–7500 p.s.i.g. for a period of 0.5 minute to one hour.

3. A process in accordance with claim 1 wherein subsequent to the displacement reaction with butylene, ethylene is removed from the displacement reaction product mixture and  $C_4$ – $C_{14}$  olefins are separated from tributyl aluminum and  $C_{16+}$  olefins.

4. In a process for producing olefins wherein triethyl aluminum is reacted with ethylene to form a trialkyl aluminum growth product and the alkyl groups of said trialkyl aluminum growth product are converted to the corresponding olefins by reaction with butylene in a first displacement reaction and  $C_{14}$  and lighter olefins are separated from the tributyl aluminum formed in said first displacement reaction and higher olefins, the improvement which comprises subsequently reacting the mixed tributyl aluminum and  $C_{16}$  and heavier olefins with ethylene to form triethyl aluminum admixed with  $C_{16}$  and higher olefins and separating said  $C_{16}$  and higher olefins from the resultant triethyl aluminum by distilling said triethyl aluminum overhead.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

2,781,410	2/1957	Ziegler et al.	260—683.15
2,863,896	12/1958	Johnson	260—683.15
2,889,385	6/1959	Catterall et al.	260—683.15
2,906,794	9/1959	Aldridge et al.	260—683.15

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