

United States Patent

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[45]	Patented	Mar. 2, 1971
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[56]

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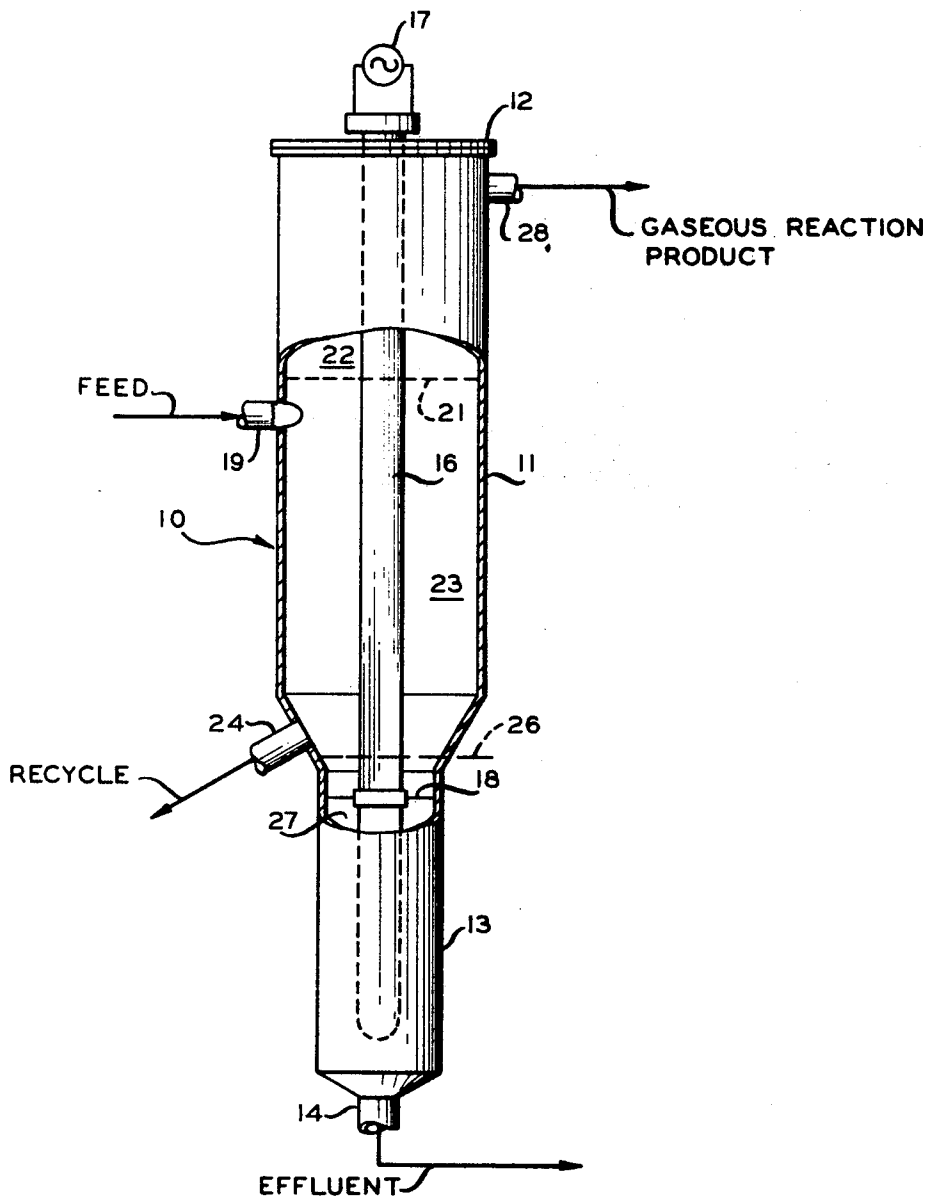
**[54] APPARATUS FOR THE CONTINUOUS
PHOTOHALOGENATION OF HYDROCARBONS
9 Claims, 5 Drawing Figs.**

[52] U.S. Cl..... 250/45,
250/43, 250/48

[51] **Int. Cl.**..... G01j 3/42

[50] **Field of Search**..... 23/285;
204/162, 163, 193; 250/43, 45, 46, 48

ABSTRACT: A photohalogenation apparatus having a gas liberation region above a reaction region, a gas outlet, a feed inlet and a product recovery outlet. A light source is associated with the reaction region to promote the halogenation reaction. Reactants flow downwardly in the vertical apparatus; the halogenated product being recovered from the lower portion of the apparatus.



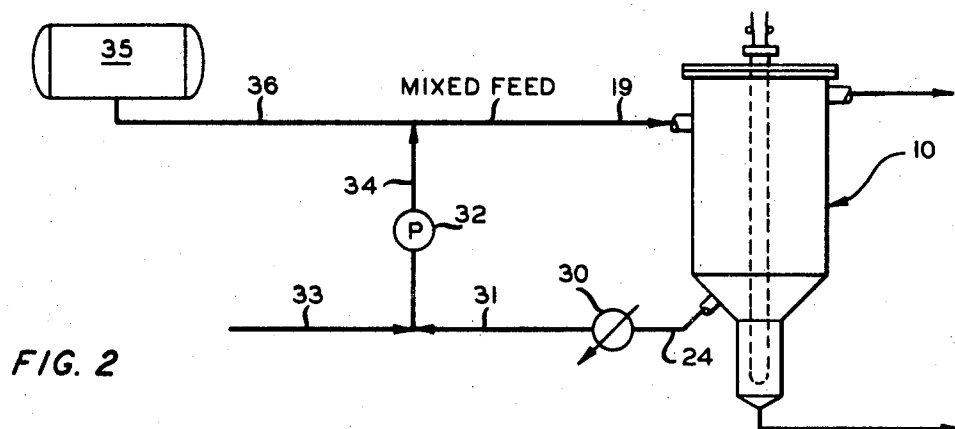


FIG. 2

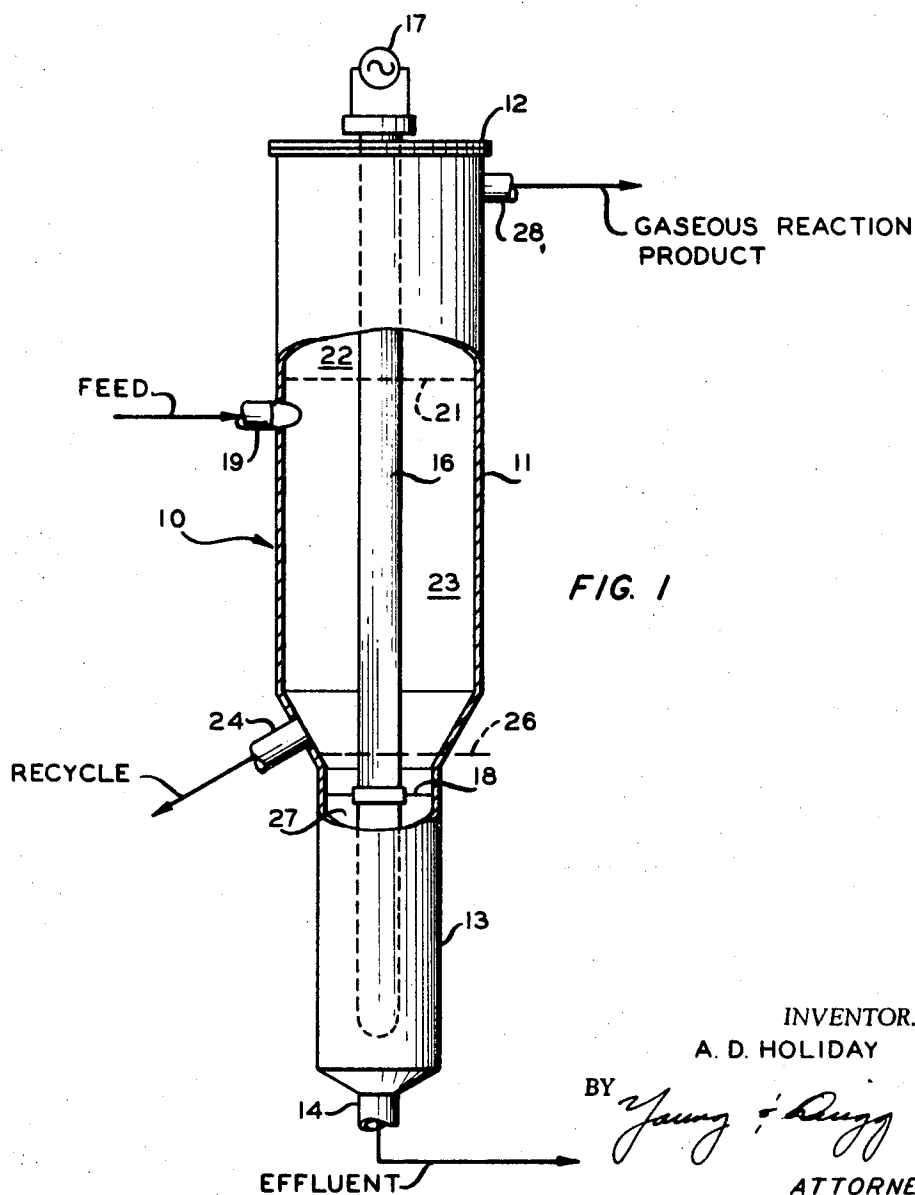


FIG. 1

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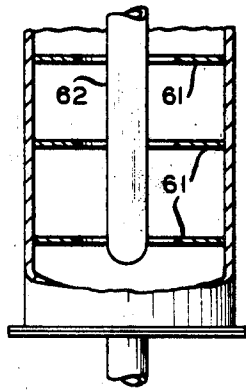


FIG. 5

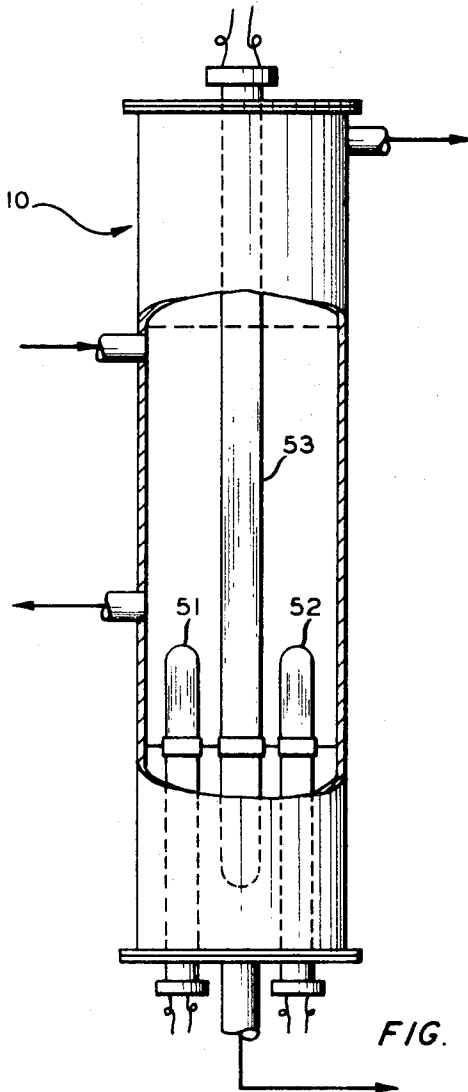


FIG. 4

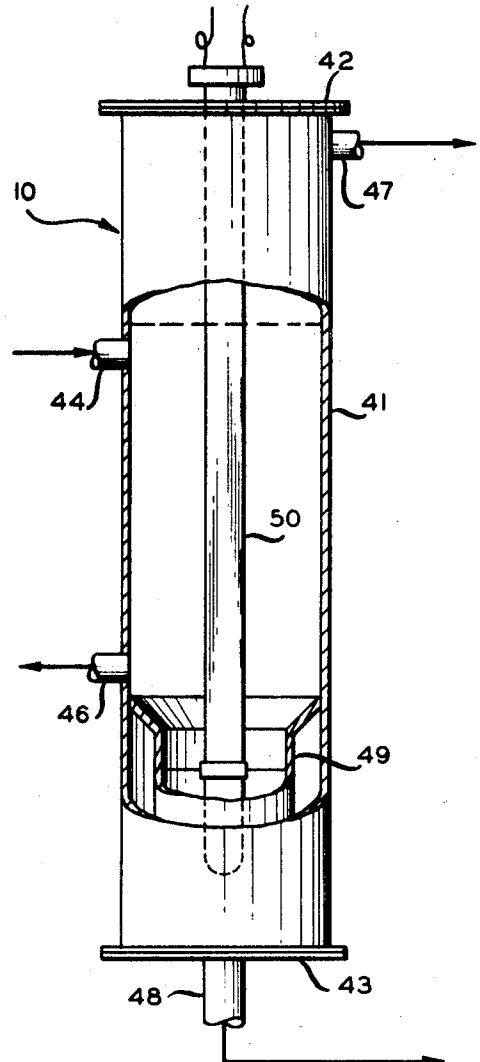


FIG. 3

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APPARATUS FOR THE CONTINUOUS PHOTOHALOGENATION OF HYDROCARBONS

This is a division of application Ser. No. 614,932, filed Feb. 9, 1967.

This invention relates to the photohalogenation of hydrocarbons. In one aspect the invention relates to a method of producing a high yield of a desired halogenated hydrocarbon derivative. In another aspect the invention relates to a photochemical reaction apparatus.

In some direct hydrocarbon halogenation methods, light of a suitable wave length is used to promote the reaction of the hydrocarbon and the halogen. These processes are sensitive to the presence of oxygen and other impurities which inhibit the action of the light and it is often necessary to provide supplemental quantities of light over that theoretical amount necessary to promote the reaction in order to obtain an economic yield.

At high conversion rates in a direct halogenation process, the monohalogenated derivative formed in the first stages of the reaction reacts with the halogen to produce more highly halogenated derivatives. Thus, in operations where it is desired to obtain high yields of the monohalogenated derivative, it is necessary to limit the rate of conversion.

It is an object of this invention to halogenate hydrocarbons.

Another object of this invention is to produce high yields of monohalogenated hydrocarbons at a relatively high rate of conversion.

Another object of this invention is to provide a single stage reaction vessel for photohalogenating hydrocarbons.

Another object of this invention is to provide a photohalogenation process which is relatively tolerant to the presence of oxygen and other impurities.

These and other objects will be apparent to one skilled in the art upon consideration of the following specification, drawings, and claims.

FIG. 1 illustrates one embodiment of the apparatus of the invention.

FIG. 2 illustrates the apparatus of FIG. 1 in conjunction with a preferred feed and recycle system.

FIG. 3 illustrates another embodiment of the apparatus of the invention.

FIG. 4 illustrates another embodiment of the apparatus of the invention.

FIG. 5 illustrates another embodiment of the structure of the reaction completion region.

According to the invention, there is provided a photohalogenation reactor comprising a vertical pressure vessel having a gas liberation region in the upper portion of the vessel, a reaction region in the mid and lower portion of the vessel, a suitable light source to promote halogenation in the reaction region of the vessel, means for introducing premixed feed into the reaction region, means for removing gaseous reaction products from the gas liberation region and means for removing the liquid reaction products.

Further, in accordance with the invention, there is provided a reactor comprising a vertical pressure vessel having a gas liberation region in the upper portion of the vessel, an initial reaction region in the midportion of the vessel and a reaction completion region in the lower portion of the vessel.

Further in accordance with the invention, associated with the reaction vessel are means for removing and recycling a portion of the partially reacted reactants to be mixed with the feed.

Further in accordance with the invention, a mixture of a halogen and a hydrocarbon is introduced into the reaction region of a halogenation zone wherein downflow mixing conditions are maintained; light of suitable wave length and intensity is supplied to promote the halogenation reaction; gaseous reaction products are recovered from a gas liberation region of the halogenation zone above said reaction region and products from the completion of the halogenation reaction are recovered from a lower portion of the halogenation zone

below said reaction region. A portion of the partially reacted feed mixture can be removed from the lower portion of the reaction region, cooled to desired temperature, and recycled to the feed mixture.

The light source can be exterior to the vessel or can be disposed within the vessel. When an exterior light source is used, the vessel can be fabricated from any suitable transparent material, such as glass or quartz, or of opaque material, such as metal, and have transparent windows through the walls thereof for the admission of light. When the light source is disposed within the vessel, the vessel can be constructed of any suitable material, for example, Monel metal, nickel or glass-lined steel.

The gas liberation region is defined by the top of the vessel and the liquid level of reactants in the vessel, the upper limit of the reaction region being defined by the liquid level of the reactants which will rise above the feed inlet means, and the lower limits of the reaction region being defined by the bottom of the vessel. When a portion of the partially reacted reactants are recycled, the recycle outlet means defines the lower limits of the initial reaction region and the upper limits of a reaction completion region.

To ensure that the reaction is catalyzed substantially uniformly during the reaction, mixing is provided in the reaction region. The mixing can be mechanically induced, for example, by stirring devices, or can result from reactant flow patterns in the reactor. It is preferred to provide for mixing by introducing the premixed feed tangentially at sufficient velocity to create a downward helical flow pattern while catalyzing the reaction under conditions resulting in the evolution of gases during the reaction, thus creating turbulence. The reaction region can be of sufficient size to allow substantial completion of the reaction.

The reaction completion region functions to react the remaining halogen with the hydrocarbon so that the halogenated hydrocarbon product is substantially free of any unreacted halogen. This can be effected by balancing the residence time in that region with the intensity of light supplied to the region. Extra light sources can be disposed in the reaction completion region so as to more rapidly promote the final reaction, or the reaction completion region can comprise a zone which is of reduced annular space so that the light does not travel as great a distance through the liquid. If desired, baffles can be employed to direct the flow of the liquid into proximity with the light source to effect completion of the reaction.

Hydrogen halide, evolved during the halogenation reaction, passes upwardly through the downwardly flowing liquids and disengages from the liquid in the gas liberation region. These vapors are removed from the gas liberation region at a rate which eliminates any danger of explosion.

Referring now to FIG. 1 the photohalogenation reactor 10 is depicted as having a cylindrical shell comprising a larger diameter 11 with a top plate 12 and a smaller diameter 13 containing an outlet 14 in the bottom. An ultraviolet light source 16 extends through a central opening in top 12 into the reaction regions. The housing of the light source can be of any suitable material, such as glass or quartz, which is heat resistant, inert to halogens and transparent to light. Lamps can be employed to provide light having a wave length of about 2000 to 7000 Angstrom units. Any suitable power source 17 can be used to energize light source 16. Guides 18 position the light source 16 stably within reactor 10. Premixed feed is introduced into reactor 10 through conduit 19. Conduit 19 enters reactor 10 tangentially so that the feed can be introduced to create a downward helical flow pattern in the reactor and provide mixing. The liquid level 21 of the reactors, above the entry point of conduit 19, determines the lower limit of a gas liberation region 22 and the upper limit of an initial reaction region 23. During the photohalogenation reaction, the reactants flow downwardly and a portion of the partially reacted reactants is removed via conduit 24 to be recycled as shown in FIG. 2. The point at which conduit 24 is positioned, as shown

by phantom line 26, defined the lower limits of initial reaction region 23 and the upper limit of a reaction completion region 27.

Reaction completion region 27 is shown as being contained within the lesser diameter 13 thus reducing the distance the light must be transmitted through the liquid and increasing the effectiveness of the light in catalyzing the reaction of any free halogen. Liquid halogenated effluent is removed via outlet 14 and transferred to various separation and/or process steps. Gaseous reaction products evolved during the halogenation are removed from gas liberation region 22 through conduit 28.

FIG. 2 illustrates one embodiment of a system for recycling the partially reacted reactants and mixing them with fresh feed constituents. The partially reacted reactants are removed from reactor 10 via conduit 24 and cooled to a desired temperature in heat exchanger 30, thus providing temperature control of the photohalogenation reaction. The amount of cooling is determined by the feed rate, recycle rate, and temperature level desired to be maintained in reactor 10. The cooled recycle portion is removed from heat exchanger 30 through conduit 31 by pump 32. Fresh hydrocarbon feed is admixed with the recycled portion in conduit 31 through conduit 33. The action of pump 32 provides for the intimate mixing of the fresh hydrocarbon feed with the recycle portion. Pump 32 transfers the mixture of fresh hydrocarbon and recycle through conduit 34 to conduit 19. Fresh halogen feed, either liquid or gaseous, stored in tank 35 flows through conduit 36, admixing with the feed constituents in conduit 34 to form the premixed feed which is introduced into reactor 10 through conduit 19.

FIG. 3 illustrates another embodiment of photochemical reactor 10 having a cylindrical shell 41, a pressure sealed top 42 and bottom 43, a feed conduit 44, a recycle conduit 46, a gas recovery conduit 47, and liquid product recovery outlet 48. The reaction completion region, defined by the position of recycle conduit 46 and bottom 43, contains a sleeve 49 to reduce the annular space between the cylindrical shell source and lamp 50 to ensure promotion of the complete reaction. If desired the sleeves may be fabricated so that they are adjustable thus allowing the annular space to be varied providing for different residence times in reaction completion region.

FIG. 4 illustrates a photochemical reactor 10 in which the reaction completion region is provided with a plurality of lamps 51 and 52 in addition to the primary light source 53 to ensure the completion of the reaction.

FIG. 5 depicts the reaction completion zone as containing a plurality of circular baffles 61 disposed in planes horizontal to light source 62 to direct the flow of the liquid in proximity with the light source.

Often it is desirable to chlorinate or brominate cyclic or acyclic hydrocarbons having 4 to 20 carbon atoms per molecule. Practice of the method and use of the apparatus of

this invention results in high yields of the monohalogenated derivative at relatively high conversion rates without the expensive duplication of equipment necessary in conventional halogenating practices. In addition, halogenation can be carried out at oxygen impurity contents not feasible in conventional practice.

The following examples will serve to further illustrate the invention.

EXAMPLE I

For pilot plant tests, a reactor as shown in FIG. 1 was constructed of a Pyrex glass tube with an upper 2-inch diameter and a lower 1-inch diameter. Two 250-watt ultraviolet lamps were mounted external to the reactor at a distance of about 3 inches. These lamps emitted light in the range of about 2000 to 6000 Angstroms. Using the feed system illustrated in FIG. 2, a premixed feed comprising liquid cyclohexane, gaseous chlorine, and partially reacted recycled reactants was introduced into initial reaction region 23 of reactor 10. The gaseous chlorine went into solution, providing a completely liquid feed. The amount of recycle liquid was varied during different runs. The recycled portion was cooled to provide a premixed feed temperature of 100° F. when added to the fresh feed constituents. The liquid reaction product was recovered from reaction completion region 27 at a rate of about 4.4 gallons per hour and analyzed to determine its composition. Hydrogen chloride gas was recovered from gas liberation region 22. The conditions, effluent analysis, and results of the different runs are tabulated below.

It can be seen that a single stage reaction carried out in the downflow reactor of this invention resulted in an average of 25.6 percent conversion of the cyclohexane to a chlorinated derivative having an average ratio of 9.1 mols monochlorocyclohexane to 1 dichlorocyclohexane mol. The reaction can be carried out at pressures in the range of atmospheric pressure to 200 p.s.i.g., temperatures of from 0° F. to 250° F. and at a volume recycle ratio of from 1 to 1 to 30 to 1 of recycle component to fresh hydrocarbon feed.

For comparison cyclohexane was chlorinated in an adiabatic upward flow photochlorination reactor which did not contain the different regions and in which there was plug flow as opposed to the mixed flow in the reactor of this invention.

A single pass in the adiabatic plug flow reactor resulted in a 12 percent conversion with a 14 to 1 monochlorocyclohexane to dichlorocyclohexane ratio, while a second pass of the effluent through the same reactor (simulating a two-stage reactor) resulted in a 24 percent conversion with a 7 to 1 monochlorocyclohexane to dichlorocyclohexane ratio.

Thus, it can be seen that photochlorination of cyclohexane in the reactor of this invention produces in a single stage a greater percent conversion with a greater quantity of

TABLE 1

	Flow line No.	Run No.					
		1	2	3	4	5	6
Conditions:							
Chlorine feed rate, lb./hr		5.9	6.2	6.5	6.4	6.7	6.6
Cyclohexane feed rate, g.p.h		4.4	4.4	4.4	4.4	4.4	4.4
Recycle rate, g.p.h		13.2	26.4	26.4	26.4	39.6	39.6
Ratio, recycle/feed, vol		3:1	6:1	6:1	6:1	9:1	9:1
Reactor feed temp., ° F		100	100	100	100	100	100
Reaction temp. ¹		160	149	149	149	138	138
Reactor pressure, p.s.i.g.		8	8	8	8	8	8
Residence time in initial reaction region, sec		25.0	14.3	14.3	14.3	10.0	10.0
Residence time in reaction completion region, sec		27.8	27.8	27.8	27.8	27.8	27.8
Effluent analysis, glc. wt. percent:							
Lights		0.3	0.2	0.4	0.4	0.3	0.2
Cyclohexane		71.1	68.0	66.3	66.5	63.4	64.1
Monochlorocyclohexane		24.4	28.2	29.1	28.4	32.2	30.9
Dichlorocyclohexane		4.1	3.5	4.0	4.4	3.9	4.6
Heavies		0.1	0.1	0.2	0.3	0.2	0.2
Results:							
Conversion of feed, percent		21.6	24.4	26.8	25.3	28.2	27.6
Mono/dichloride mol ratio		7.7	10.0	9.4	8.3	10.7	8.7

¹ As measured at recycle outlet.

monochlorocyclohexane in the product than does a two-stage reaction carried out in a plug flow reactor, a type of reactor conventionally used in many halogenation processes. Monochlorocyclohexane can be dehydrohalogenated to obtain cyclohexene, a useful olefin.

EXAMPLE II

Cyclohexane was chlorinated using the reactor and the light source described in Example I, and the feed system illustrated in FIG. 2. Air was injected into the discharge of recycle pump 30 at various rates to test the effect of oxygen inhibiting. The amount of free chlorine in the hydrogen chloride gas product and the liquid chlorinated product was determined. The table below presents the results of runs made with differing recycle and air injection rates.

TABLE 2

	Run No.				
	1	2	3	4	5
Chlorine feed rate, lb./hr.	10.0	6.4	6.4	6.4	6.4
Cyclohexane feed rate, g.p.h.	7.0	4.4	4.4	4.4	4.4
Ratio, recycle/feed rate	6:1	6:1	6:1	9:1	9:1
Feed temp., ° F	100	100	100	100	100
Air injection, s.c.f.h.	0.185	0.04	0.16	0.168	0.233
O ₂ equiv. in Cl ₂ , p.p.m.	331	107	428	450	618
O ₂ in total feed, p.p.m.	8.54	2.76	11.1	8.67	11.9
Analyses, p.p.m. wt.:					
Cl ₂ in chlorocyclohexane product	3.2	0.44	3.4	0.43	0.30
Cl ₂ in hydrogen chloride gaseous product		84	1,500	6,000	

The conversion rates and monochloro to dichloro ratios were equivalent to those obtained in Example I. It can be seen that a satisfactory liquid product can be made by oxygen levels above 600 parts per million in the chlorine feed. The maximum tolerable amount for plug flow adiabatic reactors is about 100 parts per million of oxygen in the chlorine, which is less than the 200 parts per million level of oxygen in commercial chlorine. The high oxygen tolerance of the reactor of this invention is not completely understood but it is believed that liberation of hydrochloric acid gas and its upward passage through the liquid purges the liquid phase of the oxygen and allows the chlorination reaction to be completed without excessive supplemental quantities of light.

EXAMPLE III

Normal heptane was chlorinated in the reactor of this invention with air being introduced at the discharge of recycle pump 30 shown in FIG. 2. Runs were made at various feed and recycle rates, temperatures, and air injection rates. The conditions and results of these runs are tabulated below:

TABLE 3

	Run No.				
	1	2	3	4	5
Conditions:					
Chlorine feed rate, lb./hr.	5.4	3.6	3.7	3.6	4.9
Normal heptane feed rate, g.p.w.	4.4	3.0	3.0	3.0	5.0
Recycle rate, g.p.h.	26.4	18.0	18.0	18.0	30.0
Ratio, recycle/feed, vol.	6:1	6:1	6:1	6:1	6:1
Reactor feed temp., °F.	100	100	100	100	98
Reaction temp., °F.	142	143	144	144	139
Reactor pressure, p.s.i.g.	8	20	20	20	20

TABLE 3—Continued

		Run No.				
		1	2	3	4	5
5	Residence time in initial reaction region, sec.	14.3	21.0	21.0	21.0	12.6
	Residence time in reaction completion region, sec.	27.8	40.8	40.8	40.8	24.5
	O ₂ Equivalent in Cl ₂ feed, p.p.m.	None	283	554	567	415
Results:						
	Conversion of feed, percent.	23.8	23.5	24.0	23.6	19.2
10	Cl ₂ in chloroheptane product, p.p.m.		4.4	2.3	8.1	1.5
	Cl ₂ in hydrogen chloride gaseous product, p.p.m.		321	223	222	163

It can be seen that the single stage reaction resulted in an average 22.8 percent conversion of the normal heptane to a chlorinated derivative. Further, the injection of oxygen into the system did not retard the reaction or leave excessive unreacted chlorine in the product. The chloroheptane product can be used for producing alkyl aromatics by alkylation or can be dehydrohalogenated to obtain an olefin.

EXAMPLE IV

A mixture of normal paraffins comprising about 10 weight percent n-decane, 30 weight percent n-undecane, 35 weight percent n-dodecane, and 25 weight percent n-tridecane was chlorinated using the apparatus and conditions set forth in Example III. The conditions and results of different runs with the normal paraffins are tabulated below:

TABLE 4

30		Run No.				
		1	2	3	4	5
	Conditions:					
	Chlorine feed rate, lb./hr.	3.0	2.9	2.8	3.4	3.4
35	Normal paraffin feed rate, g.p.w.	3.0	3.0	3.0	3.0	3.0
	Recycle rate, g.p.h.	18.0	18.0	18.0	18.0	18.0
	Ratio, recycle/feed, vol.	6-1	6-1	6-1	6-1	6-1
	Reactor feed temp., °F.	98	100	101	99	119
	Reaction temp., °F.	140	137	140	143	159
	Reactor pressure, p.s.i.g.	20	20	20	40	40
40	Residence time in initial reaction region, sec.	21.0	21.0	21.0	21.0	21.0
	Residence time in reaction completion region, sec.	40.8	40.8	40.8	40.8	40.8
	O ₂ equivalent in Cl ₂ feed, p.p.m.	None	354	797	303	299
	Results:					
	Conversion of feed, percent.	32.8	30.8	29.7	36.0	36.6
45	Cl ₂ in chloroparaffin product, p.p.m.	27.2	4.3	10.0	5.0	2.5
	Cl ₂ in hydrogen chloride gaseous product, p.p.m.	1,905	1,260	2,705	260	523

The example shows that the single stage reaction in the reactor of this invention produced relatively high conversion rates of the paraffins to chlorinated derivatives in the presence of oxygen.

EXAMPLE V

55 The data in Examples I through IV were obtained using gaseous chlorine feed. To determine the effect of liquid chlorine, runs were made chlorinating cyclohexane, normal heptane, and the mixture of normal paraffins described in Example IV with liquid chlorine using the feed system and reactor described in Example I. The conditions and results of the runs utilizing liquid chlorine are tabulated below:

TABLE 5

[illegible]

It can be seen that the single stage reaction utilizing liquid chlorine produced results comparable to the results obtained using gaseous chlorine. Utilizing liquid chlorine is advantageous in that it eliminates one source of oxygen impurities in the system.

Reasonable modification and variation are within the scope of the invention which provides a novel method of and apparatus for photohalogenating hydrocarbons.

I claim:

1. A photohalogenation reactor comprising:

- a. a vertical pressure vessel;
- b. an ultraviolet light source mounted in fixed relation with and in light communication with the interior of said vessel to promote halogenation within said vessel;
- c. means for energizing said light source;
- d. inlet means communicating with the upper mid portion of said vessel for introducing fluid feed mixture into said reactor and maintaining a liquid level within said reactor, said liquid level thus defining the upper limits of an initial reaction region and the lower limits of a gas liberation region within said vessel;
- e. outlet means communicating with a mid portion of said vessel for removing a portion of partially reacted reactants from said reactor, thus defining the lower limits of said initial reaction region and the upper limits of a reaction completion region;
- f. outlet means communicating with said vessel proximate to the bottom of said vessel for recovering liquid reaction products from said reaction completion region;
- g. outlet means communicating with said vessel proximate to the top of said vessel for recovering gaseous reaction products from said gas liberation region; and

h. means for maintaining the rate of reaction in the reaction completion region over the rate of reaction maintained in the initial reaction region.

2. The apparatus of claim 1 wherein said vessel comprises a cylindrical vessel.

3. The apparatus of claim 1 including means connected to said partially reacted reactant outlet means for recycling, cooling, and mixing the partially reacted portion with fresh feed constituents.

4. The apparatus of claim 1 including means for mixing the liquid reactants in the said reaction region.

5. The apparatus of claim 1 wherein said light source is mounted inside said vessel and said means for maintaining the rate of reaction of the reaction completion region comprises a plurality of vertically disposed light sources.

6. The apparatus of claim 1 wherein said light source is mounted inside said vessel and said means for maintaining the rate of reaction in the reaction completion region comprises means for reducing the space between vessel walls and said light source as compared to the space between vessel walls and said light source in the initial reaction region.

7. The apparatus of claim 6 wherein said initial reaction region and said reaction completion region are cylindrical and said reaction completion region has a smaller diameter than said initial reaction region.

8. The apparatus of claim 6 wherein said space reducing means comprises a sleeve which is adjustable to provide for altering the residence time in said reaction completion region.

9. The apparatus of claim 1 wherein said light source is mounted inside said vessel and the means for maintaining the rate of reaction in the reaction completion region comprises baffles to divert the flow of reactants in close proximity to said light source.

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