Preliminaries in Carbon ^{13}C Separation Process by Low Temperature Distillation

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***Abstract* – This paper presents an experimental plant which separates Carbon ^{13}C isotopes. Beginning with an overview of Carbon ^{13}C Separation Process, it will be presented the conventional separation column. Also, there are relatated the required procedures that are done through experimental plant of isotope separation under continuous feed.**

***Keywords:* isotopes; separation process; separation column; carbon ^{13}C; chemical exchange process**

I. BEGINNINGS OF ^{13}C CARBON SEPARATION PROCESS

Like it is mention in literature [1-2], the first grams of 13C were produced in Mound Laboratory, United States in 1960.

Since then, the presence of stable isotope 13C in diverse fields such as medicine, chemistry, biology, biochemistry, agronomy or nuclear energy contributes to innovation of these various industry fields.

In the following figure is presented the diagrammatic representation of Carbon isotopes, more precisely it can be seen different carbon isotopes such as 12C, 13C and 14C.

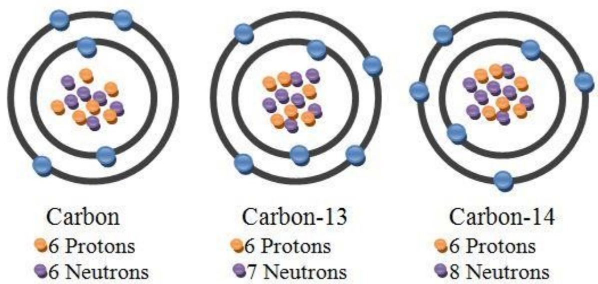

Fig. 1. Diagrammatic representation of Carbon isotopes

Some of the current methods of separation of 13C, which are also presented in literature [3-7], are the following:

- chemical exchange carbon dioxide carbamate
- low-temperature distillation of carbon monoxide termodifusion
- selective dissociation of laser radiation
- gas diffusion

Distillation is a process of balance, the energy required for this is much smaller in comparison with termodiffusion and gaseous diffusion.

The main elements of Carbon separation plant by low temperature distillation of carbon monoxide are the following:

- distillation column with high efficiency unordered filling
- capacitor with role of reflux at the top of the column
- the kettle with role of reflux at the bottom of the column

Thermal insulation of the entire system is ensured by a vacuum jacket and reflective screens, meanwhile the carbon is concentrated to base of the separation column.

Thus, energy costs are minimal both for small productions and for intermediate productions. Among the disadvantages of this process is that carbon monoxide is distillation at low temperatures. Another disadvantage is the fact that carbon monoxide is highly toxic.[1-3]

II. THEORETICAL ASPECTS ABOUT CARBON SEPARATION PROCESS

The separation of two substances with different vapor pressures is made in order to concentrate a certain substance of interest.

Due to the fact that in isotopes separation the difference between boiling points is represented by a small fraction of a degree, to extend this process to separation of isotopes the operation must be repeated very often.

The operation of separation is carried out in a fractionating column where the upward vapor stream is brought into intimate contact with a descending liquid stream. The liquid is vaporized at the bottom meanwhile the vapor is condensed at the top.

At the same time, there is an exchange of molecules between the two phases, more precisely the component more volatile move preferentially in the vapor phase and then it tends to accumulate itself at the top of the column, meanwhile the component less volatile concentrate itself in the liquid phase and tend to accumulate at the bottom of the column.

Separation coefficient is noted with α and is given by the ratio of pure isotopic components pressure. Also, in the following ecuation can be seen the representation of the separation coefficient.

$$\alpha = \frac{P_1^0}{P_2^0} \qquad (1)$$

Where:

- P_1^0 - represents the pressure of the first isotopic component;
- P_2^0 - represents the pressure of the second isotopic component;

In the following table are represented different values of α for isotopic species of interest.[1-2]

TABLE 1. Values of of separation factor α for different isotopic species

Pair	Temperature (ºK)	α-1
$^{12}C^{16}O/^{13}C^{16}O$	81.1	0.0070
$^{12}C^{16}O/^{13}C^{16}O$	68.3	0.0109
$^{12}C^{16}O/^{12}C^{18}O$	77,0	0,0059
$^{12}C^{16}O/^{12}C^{18}O$	69,0	0,0079

Thus, if a mixture of two species of isotopes whose ratio of the vapor pressure is α, was distilled at total reflux in a column, the ration of concentration of isotope changes by a factor α per each theoretical plate, and if there are n theoretical plates, the concentration of isotope changes by a factor αn.

II. THE EXPERIMENTAL PLANT REPRESENTED BY A SINGLE SEPARATION COLUMN

It is known from literature [5-8] that the scope of isotopic separation process is to increase the concentration of an isotope in a specific environment. Also, the base of isotope separation technique is related on differences between the physical - chemical properties of the isotopes.

A. Separation column

The main important element of the separation plant is represented by the separation column, more precisely, special device which multiplies the elemental separation effect in case of isotope exchange reactions.

In [5-9] is presented the fact that the separation column contains two sections, one for enrichment and one for dilution. The feeding point of the column divides the column into enrichment section and into dilution section. Inside, the column is filled with triangular spirals made of stainless steel wire.

Inside the enrichment section, each time when separation plant is supplied with desired isotope product, the isotope's concentration is increased up to the desired value. Meanwhile, inside the dilution section, the isotope's concentration is decreased under the natural isotope concentration.

In the following figure is presented the structural scheme of an experimental plant represented by a single separation column:

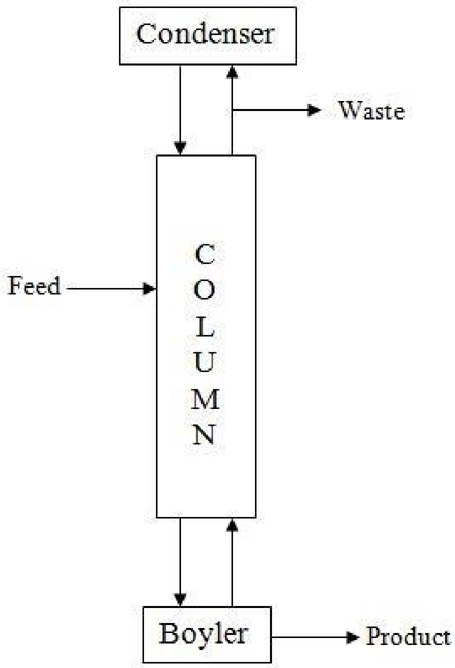

Fig. 2. Schematically representation of isotope separation plant

Also, [1-2] the most important characteristics of the isotope separation column are:

- Hold-up on plate – determine the time to reach equilibrium
- HETP – height equivalent theoretical plates – determines the height of the column to achieve a certain separation
- permitted load – separate product flow is directly proportional to the load
- pressure drop across the plate – as small as possible

Like it is known from literature [1-2, 6-8], the requirements that should be fulfilled by a separation column are the following:

- high load
- small hold-up
- low pressure drop
- small HETP

B. *Other components of the plant*

As it is mentioned in the literature [9-12], besides separation column, other main components of experimental isotopic separation plant are the following:

- the condenser
- the kettle (boiler)
- the vacuum jacket
- the vacuum aggregates

The condenser, which is made of stainless steel, provides reflux to the top of the column by total condensation of carbon monoxide, using liquid nitrogen boiling at atmospheric pressure.

Also, the condenser is cylindrical and is provided with longitudinal fins to increase heat exchange surface. The liquid flows by gravity from condenser on the filling of the column in countercurrent with carbon monoxide gas.

The kettle, which is placed at the base of the column, ensures backflow of liquid carbon monoxide. The kettle is heated with an electrical resistance.

The plant is constructed of stainless. Also, the whole plant is isolated and inserted into a vacuum jacket. The vacuum is achieved with two vacuum units, more precisely preliminary vacuum pump and oil diffusion pump, located at the ends of the installation.

Meanwhile the sampling is done on carbon monoxide, the isotopic analysis is performed with a mass spectrometer.

IV. THE PROCEDURES REQUIRED IN ^{13}C CARBON SEPARATION PROCESS

As the literature mentions [1-4], there are multiple required procedures that should be fulfilled in order to obtain the final product of ^{13}C Carbon.

A. *Prerequisites in ^{13}C Carbon separation process*

Before starting the Isotope Separation Process, there is needed to perform a set of actions such as [1-2]:

- checking the tightness of the shell of isolation by vacuum
- checking the tightness of the plant
- checking the residual pressure
- vacuuming the plant and all its links
- checking all gauges and valves
- checking the liquid nitrogen supply system
- connecting the plant with carbon monoxide cylinder
- checking the pressure in the cylinder and buffer vessel
- connecting the vessel with liquid nitrogen supply system

After performing these actions, the carbon monoxide is introduced into the plant after the condenser starts cooling with liquid nitrogen. Also, the separation column is cooled as the carbon monoxide liquefies and accumulates itself in the plant.

Another thing is the fact that the heating of the kettle switches to rated power to achieve the desired load of the column when the liquid carbon monoxide reaches at the bottom of the column.

Samples are taken both from the bottom of the column and the top of the column and, if necessary, from the supply point and analyzed by mass spectrometry.

B. *Automated plant for ^{13}C Carbon separation process*

The use of an automated plant [11-14] is necessar for maintaining the relation between feed flow rate, the product flow and the exhaust flow waste. These flows must comply with the relation:

$$F = P + W \qquad (2)$$

Where:

- F - feed flow rate
- P - the product flow
- W - the exhaust flow waste

The automated plant, also described in literature [11-14] is based on measuring the level of liquid in the kettle of the column and transmits information to control elements that will cause flow variations to a discharge waste pump.

The necessary conditions for the automated loop to work properly are the following:

- the vacuum pressure in the shell should be as low as possible and also constant in order to permit a very small heat transfer from the outside
- the injected power to electric heater of the boiler must be constant, otherwise both the molar flow rate of the column and the liquid level from the kettle cup will be variable
- quality of carbon monoxide must be very good, otherwise, the impurities will be accumulated at the supply point
- the level of liquid nitrogen from condenser must be constant in order to ensure a uniform reflux to the top of the column

C. *The experimental process of ^{13}C Carbon separation*

Like it was mention before [1-3], the necessary operations that has to be done in order to perform the separation process are the following:

- preparing the necessary quantity of carbon monoxide for the experiment

- wetting the filling by complete flooding the distillation column with liquid carbon monoxide
- extracting the surplus of carbon monoxide from the plant
- supplying the plant with carbon monoxide at natural concentration meanwhile the waste is discharged

Like it is mention in literature, [1-2] the column is feed from a point located above the top of the column. Feed rate is depending not only on the size of the column, but also on operating parameters and performance of the separation column. Also, it is necessary to take samples from the feed point before starting the feed or extraction of the waste.

The operation of a cryogenic distillation of carbon monoxide under productive regime involves continuous feeding of the column with carbon monoxide whose 13C content has the natural concentration.

The extraction of the enriched in 13C product of the column is made at the bottom of the column meanwhile the discharge of diluted in 13C waste is made at the top of column.

Disposal of the waste is achieved with a diaphragm pump whose speed is variable and which is controlled according to the level of liquid in the kettle's glass.

V. CONCLUSIONS

Since 1960 it is known the major contribution of stable isotope ^{13}C in various fields of industry such as chemistry, biology, medicine, agronomy or nuclear energy and also how it innovats areas of industry.

In order to perform the separation process, it is required various prerequsites actions. The operation of a cryogenic distillation of carbon monoxide involves continuous feeding of the column with carbon monoxide whose ^{13}C content has the natural concentration.

As a result of the process, the extraction of the enriched in ^{13}C product of the column is made at the bottom of the column meanwhile the discharge of diluted in ^{13}C waste is made at the top of column.

Due to the fact that enrichment carried out in a single column is insufficient, to obtain better results, it is necessary to use multiple columns in series.

For a given separation, there is the possibility to used more columns in series having decreasing diameters from feed point to the end product with the corresponding decrease in flow rate.

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