

Numerical modeling of oil gas adsorption on activated carbon

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Abstract

This article aims to present the numerical modeling of the adsorption of rich gases (propane, butane, hexane) from wellhead gazelles associated with oil and gas fields. Descriptive elements of the rich gas desorption by natural gas plant are shown and later the effects of the passage of these gases on activated carbon structures are presented.

Keywords: Gas desorption, liner modelling, propane, butane, hexane.

Date of Submission: 02-12-2024

Date of acceptance: 11-12-2024

I. INTRODUCTION

The processes for removing rich gases from commercial gas (methane and ethane) are based on the selective adsorption capacity of activated carbons of hydrocarbons with a higher molar mass from natural gases.

Selective adsorption capacity is given by [1]:

- the adsorption or loading capacity of coal (expressed in kg of adsorbed hydrocarbons/100 kg of coal),
- the nature of the adsorbed hydrocarbon (by its molar mass),
- the remaining (equilibrium) partial pressure of the adsorbed hydrocarbon.

In practice, it has been observed that at the same partial pressure of the hydrocarbon (for example, 400 bar), the adsorption capacity of n-butane on coal is much higher than that of ethane (20 kg butane C₄/100 kg activated carbon compared to 5.5 kg ethane C₂/ 100 kg of coal).

It was also found that increasing the temperature significantly reduces the adsorption capacity, so adsorption must be carried out at normal temperatures [2].

The rich gas recovery (desorption) by natural gases by adsorption on activated carbon is known to be carried out by:

- the classic procedure based on four successive operations (Four times);
- the process based on two successive operations (thermos-adsorption or the Nicolae Petcu process [3]).

Regardless of the procedure adopted, the respective operations take place in adsorbers, which are vertical cylindrical vessels with a diameter of 1.5...2.5 m and a height of (2...2.5) times greater than the diameter.

They are provided on the inside with a fixed layer of active carbon.

If we take into account the classic four-time adsorption process, the four operations are [4,5,6,7]:

- the actual adsorption operation of hydrocarbons on coal, which lasts 10...30 minutes;
- the desorption operation of the hydrocarbons adsorbed in the first operation which lasts 7...15 minutes;
- the coal drying operation that lasts for 5...7 minutes;
- the coal cooling operation for which 5...7 minutes are needed.

Only the first of the four times represents the device's productive time compared to the flow of natural gas.

The other times (times 2, 3, and 4) actually represent the times required to regenerate the carbon layer in the adsorber in order to resume a new adsorption cycle: desorption, drying, and cooling.

The sum of these times is different depending on the amount of coal and the gasoline content of the gases.

Usually, the adsorption time is double the sum of the other times.

Suppose the time required for the adsorption operation is equal to the sum of the other three regeneration times of the carbon in an adsorber.

In that case, a module of two adsorbers is required to achieve a continuous rich gas recovery (desorption) process.

But if the four times are equal, a module of four adsorbers is necessary to achieve a constant rich gas recovery (desorption).

Considering the actual times recorded in industrial rich gas recovery (desorption) processes, even a module of three adsorbers is usually sufficient to carry out a continuous process.

Regardless of the number of adsorbers in the module (three or four), a complete cycle's four operations (phases) follow in the order presented above for each adsorber.

Also, due to the restrictions regarding the maximum diameter of the adsorber, two, three, and even four modules are used in parallel to increase rich gas recovery (desorption) capacity to the natural gas so that a normal adsorption-desorption installation can appear with 12...16 adsorbers.

The actual adsorption operation or phase is carried out by successively supplying natural gas to each adsorber in the module on the lower side.

The adsorption, respectively, and the feeding of the adsorber with natural gas continue until the concentration of the so-called key hydrocarbon (usually propane) reaches a predetermined value in the lean gas (desorbent) that leaves the adsorber at the base.

This preset value corresponds to the so-called breaking point, which can be defined either as the time required to feed the adsorber at a certain gas flow rate or as the volume (quantity) of gas that must feed the respective adsorber provided with a certain mass of coal until the flow of lean gas appears to be the preset concentration of the key component.

This breaking point is determined experimentally and depends both on the quality of the coal and especially on the gasoline content of the natural gas.

As this content changes over time, it is recommended that the breaking point be determined again after certain periods of installation operation.

After the adsorption operation, each adsorber is subjected to the desorption operation [5,6,7].

This operation is performed with medium-pressure steam (4...6 bar) superheated to 250...300°C.

In this operation, steam (1) is introduced in the opposite direction to the introduction of natural gas during adsorption (so from top to bottom) to avoid circulating the entire amount of desorbed hydrocarbons with a higher molar mass along the entire coal layer, as these hydrocarbons are mostly adsorbed at the base of the adsorber.

The gas occupying the free space between the coal granules is first removed by introducing steam.

After the steam passes through the entire layer of coal, the evacuation of gases can be considered finished.

Starting from this moment, the desorption of the adsorbed hydrocarbons takes place, and a mixture of hydrocarbon vapors and steam emerges from the adsorber.

This mixture successively passes through condensers 1 and 3, respectively, through separators 2 and 4, where water, gasoline, and a flow of vapors are separated (gas) that goes to a compressor.

The experimental data show that about 80% of the steam consumed during desorption remains on the charcoal, substantially reducing its adsorption capacity.

Therefore, to restore the adsorption capacity, the steam remaining in the adsorber in the form of condensate must be removed. This is done by operating the drying phase with lean (rich gas recovery (desorption) process) gases heated to 120 ... 140°C in the steam preheater 5.

After drying, the coal remains at a high temperature, significantly reducing its adsorption capacity.

For this reason, the operating cycle of an adsorber is completed with its cooling phase, which uses lean gases resulting from the process and bypasses the steam preheater 5.

After drying and cooling (so before resuming the adsorption operation), the carbon in the adsorber still contains a moisture of 1...2% and has a temperature of 30°C.

In the thermoadsorption process developed by the Romanian engineer Nicolae Petcu, the adsorption operation takes place at 80...90°C, thus eliminating the drying and cooling phases.

At the same time, by increasing the adsorption temperature to 80...90°C, the capacity to load coal with gasoline can decrease by half compared to the value corresponding to the temperature of 30°C.

This lower retention of gasoline per unit mass of coal was, however, compensated by Petcu by the corresponding increase of the coal/gas mass ratio.

Thermoadsorption takes place in two phases: the actual adsorption phase, simultaneously with the partial drying of the coal as a result of the fact that when the natural gas front advances through the coal layer, which has a temperature of 80...90°C, it acts as an inert gas on the water in the adsorber, vaporizing it and partially removing it from the coal, an operation that increases its loading capacity.

For this reason, in the first minutes of the adsorption phase, the lean gases that leave the adsorber at the top are very humid, and the water vapor condenses right on the exit pipe from the adsorber. Gradually, the natural gas entering the adsorber dries the coal mass, encouraging the adsorption of hydrocarbons.

The second phase of the thermoadsorption process is desorption, which is also done with steam, as in the classic four-time process [8,9].

II. RESULT AND DISCUSSION

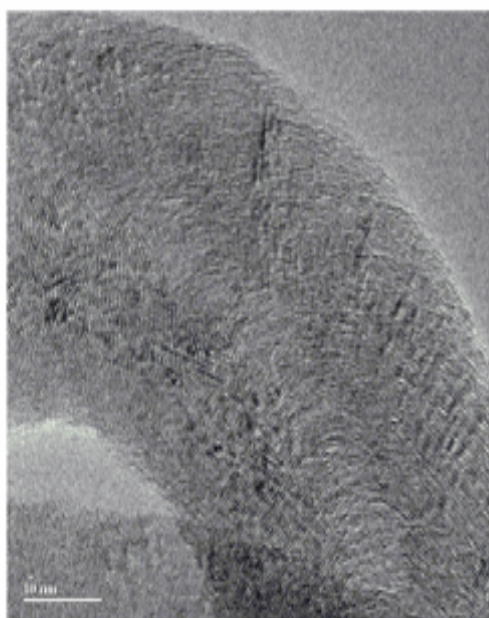
In order to observe the efficiency of adsorption on activated carbon of liquefied petroleum gases, we studied the operating parameters of a technological installation for the adsorption of petroleum gases.

We analyzed:

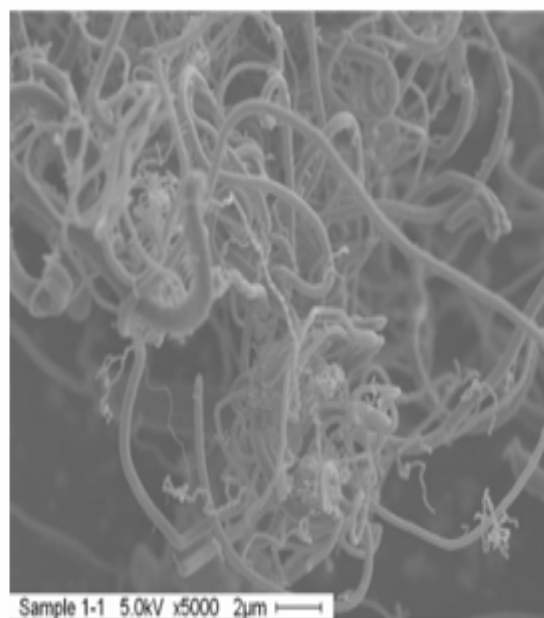
- Gas concentration at the entrance to the system (rich gas recovery (desorbtion) process plant) by analyzing the gas chromatograms provided by the beneficiary,
- Gas concentration at the exit from the system (rich gas recovery (desorbtion) process plant) by analyzing the gas chromatograms provided by the beneficiary,
- The pressure on each component.

Table 1. Inlet gas analysis

Component	Retention time, s	Area. mm ²	% Area	Concentration V	Normal concentration, V
C ₆₊	1,583	121606	1,2832	0,225	0,181
Etane	4,483	529228	6,0196	6,477	5,220
CO ₂	5,033	73954	0,8412	0,925	0,746
Propan	5,400	337596	3,8399	3,023	2,437
Isobutane	6,683	49675	0,5650	0,368	0,296
N-Butane	8,033	131698	1,4980	0,731	0,589
I-pentane	12,083	40374	0,4592	0,221	0,178
N-Pentane	14,300	43671	0,4967	0,267	0,215
Nitrogene	19,050	60421	0,68732	0,728	0,587
Methane	19,983	7403509	84,2099	111,110	89,551



a



b

Figure 1. Activated carbon before the passage of rich gases (figure A) and after the passage of rich gases (figure B)

Table 2. Product gas composition

Component	Normal	At the hourly flow rate of 133 kg/h
	Composition (%mol)	Product quantity kg
N ₂	0,51	0,6783
CO ₂	0,49	0,6517
CH ₄	89,97	119,6601
C ₂ H ₆	5,28	7,0224
C ₃ H ₈	2,15	2,8595
i-C ₄	0,26	0,3458
n-C ₄	0,78	1,0374
i-C ₅	0,16	0,2128
n-C ₅	0,19	0,2527
C ₆ H ₁₄	0,11	0,1463
C ₆ +		0
C ₇ +	0,10	0,133
H ₂ S	0,00	0
S	0,00	0
O ₂	0,00	-
H ₂ O	sate	-
Total	100,00	133

To see how activated carbon acts on petroleum gases, the amount of product entered into the column and the amount of product absorbed (by subtracting from the amount of product received in the pipeline) were studied.

Thus, at the hydrocarbon partial pressure of 100 mBar and after 24 hours of operation, the flow rates in table 3 result.

Table 3. Efiency of installation (rich gas treatment)

Component	Normal concentration before entering the installation, kg/24 h	Normal concentration after leaving the installation, kg/24 h	Amount retained in kg of hydrocarbon-100 kg of coal
Metane	2856	2856	0
Ethane	168	166	2,000
Propane	48	40	8,000
n-butane	36	20	16,000

At the hydrocarbon partial pressure of 200 mBar and after 24 hours of operation, the following operation of the installation was found.

Table 4. Efiency of installation (rich gas treatment) to the 200 mBar

Component	Normal concentration before entering the installation, kg/24 h	Normal concentration after leaving the installation, kg/24 h	Amount retained in kg of hydrocarbon-100 kg of coal
Metane	2856	2856	0
Ethane	168	164	4
Propane	48	37	11
n-butane	36	18	18

At the hydrocarbon partial pressure of 300 mBar and after 24 hours of operation, the following operation of the installation was found (Table 5).

At the hydrocarbon partial pressure of 400 mBar and after 24 hours of operation, the following operation of the installation was found (Table 6).

At the hydrocarbon partial pressure of 500 mBar and after 24 hours of operation, the following operation of the installation was found (Table 7).

Table 5. Efiency of installation (rich gas treatment) to the 300 mBar

Component	Normal concentration before entering the installation, kg/24 h	Normal concentration after leaving the installation, kg/24 h	Amount retained in kg of hydrocarbon-100 kg of coal
Metane	2856	2856	0
Ethane	168	163	5
Propane	48	35	13
n-butane	36	17	19

Table 6. Efficiency of installation (rich gas treatment) to the 400 mBar

Component	Normal concentration before entering the installation, kg/24 h	Normal concentration after leaving the installation, kg/24 h	Amount retained in kg of hydrocarbon-100 kg of coal
Metane	2856	2856	0
Ethane	168	162,5	5,5
Propane	48	34,5	13,5
n-butane	36	15,5	20,5

Table 7. Efficiency of installation (rich gas treatment) to the 400 mBar

Component	Concentratia normal inainte de intrare in instalatie, kg/24 h	Concentratia normal dupa iesirea din instalatie, kg/24 h	Cantitatea retinuta in kg hidrocarbura-100 kg de carbune
Metane	2856	2856	0
Ethane	168	162	6
Propane	48	34,5	14
n-butane	36	15	21

The evolution of the amount absorbed on activated carbon depending on the partial pressure is shown in table 8 and figure 1.

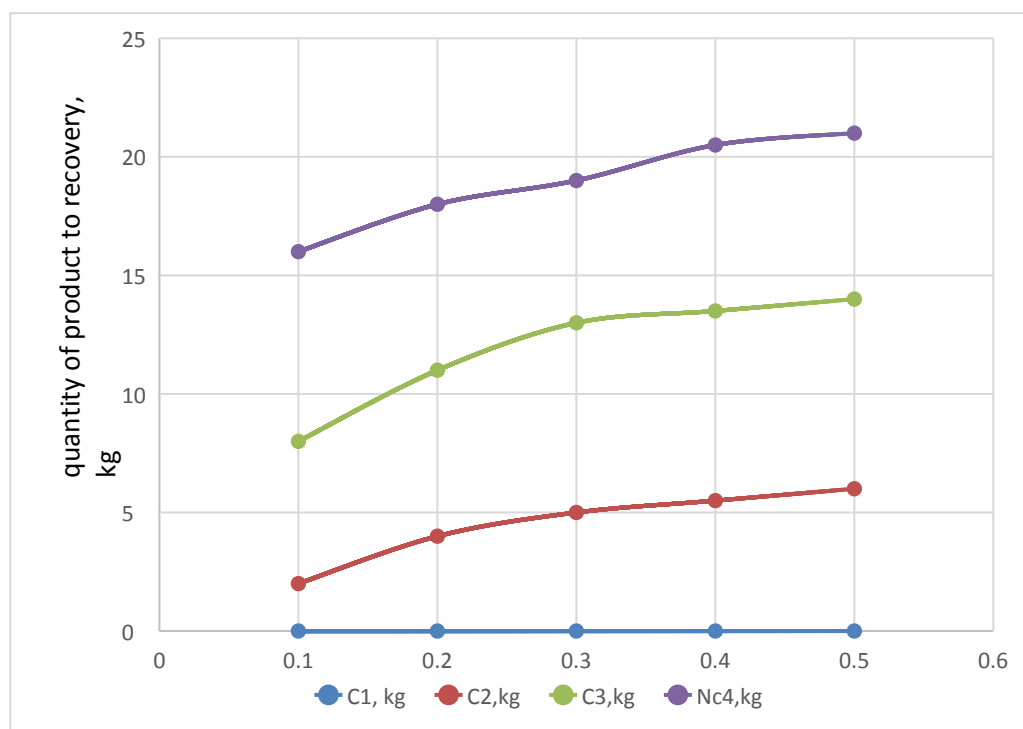


Figure 1. Efficiency of installation (rich gas treatment) to different pressure at 24 h to function

Table 8. Efficiency of installation (rich gas treatment) P, bar

Presure, bar/ Quantity of recovery after 24 h to function	0,100	0,200	0,300	0,400	0,500
C1, kg	0	0	0	0	0
C2,kg	2	4	5	5,5	6
C3,kg	8	11	13	13,5	14
Nc4,kg	16	18	19	20,5	21

In order to study the behavior of C2 adsorption as a function of pressure, we chose as a model the linear regression starting from the equation:

$$Y=a + b X \tag{1}$$

For all the above data we determined the equations through a Matchad model and then checked the model for appropriateness.

The equation becomes:

$$Y=1.65 +9.5X \tag{2}$$

Where Y is the amount of C2 retained by the coal and X is the pressure in barr.

Table 9. Analysis of models to C2 recovery (measurement and equation analysis)

Pressure, bar	Quantity of C2, measurement, kg	Quantity of C2 function by equation,kg
0,1	2	2,6
0,2	4	3,55
0,3	5	4,5
0,4	5,5	5,45
0,5	6	6,4

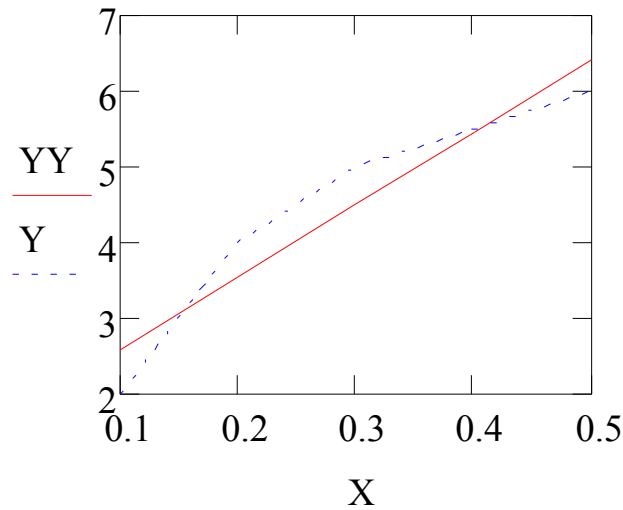


Figure 2. Evolution of the adsorption of the C2 fraction (measured Y, calculated YY) depending on the pressure X

The values of the Student distribution for this case give us the values $\alpha=0.05$ and $n = 2$ degrees of freedom are 4.303 from the table and (1.9) calculated so the model is adequate,

Also the Fisher test gives us the value 0.902 lower than 3.24 from the tables.

In order to study the behavior of C3 adsorption as a function of pressure, we chose as a model the linear regression starting from the equation:

$$Y=a + b X \tag{3}$$

For all the above data we determined the equations through a Matchad model and then checked the model for appropriateness.

The equation becomes:

$$Y=7.55 +14.5X \tag{4}$$

Where Y is the amount of C3 retained by the coal and X is the pressure in barr.

Table 10. Analysis of models to C3 recovery (measurement and equation analysis)

Pressure, bar	Quantity of C3, measurement, kg	Quantity of C3 function by equation,kg
0,1	8	9
0,2	11	10,45
0,3	13	11,9
0,4	13,5	13,35
0,5	14	14,8

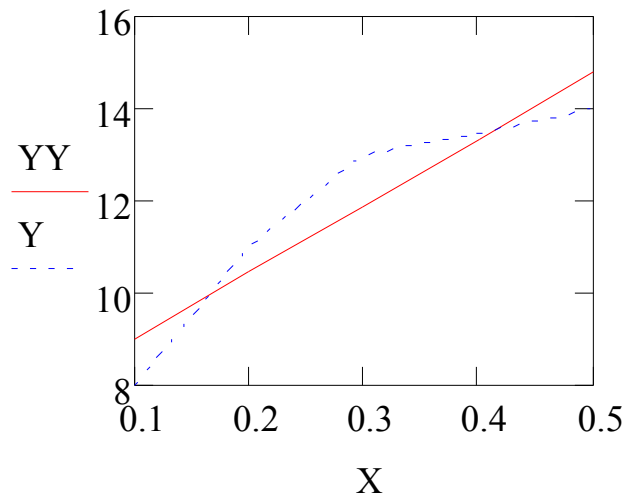


Figure 3. Evolution of the adsorption of the C3 fraction (measured Y, calculated YY) depending on the pressure X

The values of the Student distribution for this case give us the values $\alpha=0.05$ and $n = 2$ degrees of freedom are 4.303 from the table and (1.864) calculated so the model is adequate, Also the Fisher test gives us the value 0.869 lower than 3.24 from the tables. To study the behavior of C4 adsorption as a function of pressure, we chose the linear regression model starting from the equation:

$$Y=a + b X \tag{5}$$

For all the above data we determined the equations through a Matchad model and then checked the model for appropriateness.

The equation becomes:

$$Y=15.15 +12.5X \tag{6}$$

Where Y is the amount of C4 retained by the coal and X is the pressure in barr.

Table 11. Analysis of models to C4 recovery (measurement and equation analysis)

Pressure, bar	Quantity of C4, measurement, kg	Quantity of C4 function by equation,kg
0,1	16	16,4
0,2	18	17,65
0,3	19	18,9
0,4	20,5	20,15
0,5	21	21,4

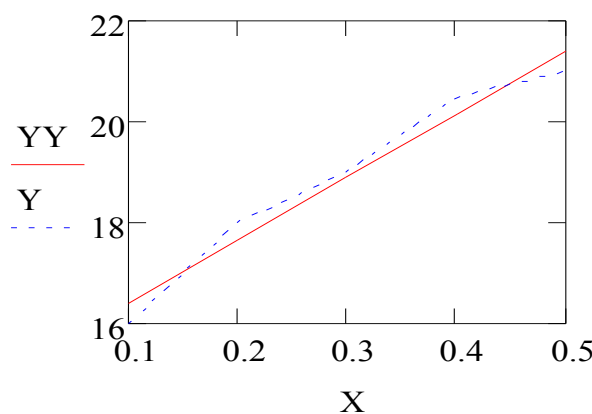


Figure 4. Evolution of the adsorption of the C3 fraction (measured Y, calculated YY) depending on the pressure X

The values of the Student distribution for this case give us the values $\alpha=0.05$ and $n = 2$ degrees of freedom are 4.303 from the table and (1.964) calculated so the model is adequate, Also the Fisher test gives us the value 0.965 lower than 3.24 from the tables.

In figure 5 we represent equation of coal adsorption capacity kg hydrocarbon/100 kg coal, (C2,C3, nC4) function to the partial pressure (mbar).

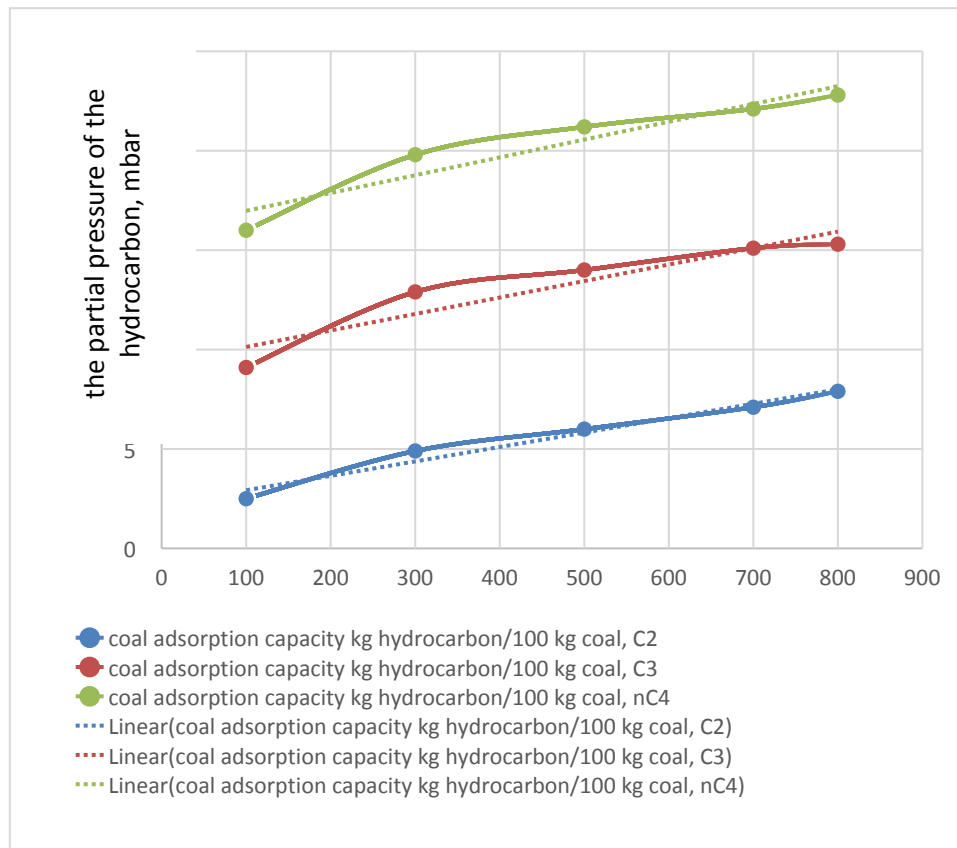


Figure 5. Equation of coal adsorption capacity kg hydrocarbon/100 kg coal, (C2,C3, nC4) function to the partial pressure (mbar)

III. CONCLUSION

At the beginning of natural gas processing, when the problem arose of recovering C4+ hydrocarbons for use as gasoline for engines, that operation was known as desalination. The resulting product was called gasoline, which, in the U.S., means gasoline.

That is precisely why, in the USA, the name rich gas is used for gasoline [2].

When the problem of recovering propane was also raised, the resulting product was found at high pressure, and for this reason, the notions of high-pressure and low-pressure gasoline appeared.

Today, when the issue of recovering ethane from natural gas is raised, the notion of desalination, respectively, of gasoline has lost its initial meaning, and that is why it has been replaced by the idea of recovering the C3+ or C2+ fraction in the latter case, the respective operation being also known as natural gas demethane.

For the rich gas recovery to the natural gases in the sense of recovery of the C3+ or C2+ fraction, several processes are known, among which are mentioned:

- compression degassing;
- the condensation process at low temperatures;
- the process of absorption in petroleum fractions;
- the process of adsorption and thermoadsorption on activated carbon;
- the procedure to recovery by fractionation at low temperatures is achieved by turboexpansion.

In the oil industry (considering that these installations are mostly made and operated by petrochemical technologists), many installations have been developed. Most of them operate according to the procedures stated above, their role being to recover the advanced C3+ and C2+ fractions and to reduce energy consumption.

Adsorption of rich gas to the activated carbon it is a good technology and friendly to the environment.

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