Salix viminalis wood as a new precursor for manufacturing of carbon molecular sieves for effective methane/nitrogen separation

Abstract: Separation of a methane/nitrogen gas mixture was investigated by means of carbon molecular sieves (CMS) obtained from a newly discovered “green” resource: Salix viminalis. This plant grows quickly, yields hard wood and is frequently cultivated for energy purposes (renewable green fuel). Unconventional applications such as charcoal fabrication using this sort of wood are very rare. Carbonization of the wood (1–3 h, 600–700°C) yields carbons with a very narrow pore size distribution (determined by N2 adsorption at -196°C) resembling a perfect CMS. The diameter of most pores (ca. 0.8 nm) is comparable to the size of simple molecules, thus enabling separation. The sieving effect was proven in an industrially important process of CH4/N2 separation at 30–70°C. Despite relatively minor differences of the size of the molecules, the experiment demonstrated that separation factors are placed in the range 3.64–10.20. Additional experiments involving krypton proved that the separation mechanism is based on a geometric factor i.e. the known size and shape of the molecules under separation.

Keywords: carbon molecular sieve, methane/nitrogen separation, Salix viminalis, carbonization

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1 Introduction

Gas mixture separation and gas storage are emerging subjects in contemporary science and technology [1,2,3]. Gas separation may proceed when a gas mixture is brought into contact with a porous solid (adsorbent). When the pores of a solid are of a proper size, one may expect that a molecular sieving effect may occur [4]. The molecular sieving effect of a porous solid is more efficient if the gas molecules to be separated are of different dimensions and when the size of the pores is comparable to the dimensions of some of the molecules to be separated. However in some cases of successful molecular separation, the average pore size approaches the sub-nanometre range which, in general, is one order of magnitude larger than the average dimensions of some simple molecules/atoms. The above statement is consistent with literature quoting the dimensions of some simple molecules and atoms in the gas phase [5,6,7] determined by experimental and theoretical methods.

Some studies point out the importance of the “geometric factor” as the main mechanism of gas separation leading to differentiated adsorption of molecules from the gas phase under static conditions like determination of adsorption isotherms [8,9]. Gas separation may also proceed under dynamic conditions when a gas mixture is passed through a membrane or along the surface of a porous solid (i.e., chromatographic column). Industry widely exploits gas separation based on differences in adsorption/desorption kinetics of particular mixture components on a porous solid as in the PSA method for air separation [10,11]. Air separation is performed on several porous solids, but zeolites [12] and active carbons [13] are most commonly applied. These two groups of adsorbents have acquired industrial approval for economic reasons, as the materials’ high functionality is achievable at relatively low cost. Simple manufacturing in large quantities is an additional positive feature. However, the literature offers reports on gas separation over other porous solids such carbon nanotubes [14], but CNTs are not accessible in large quantities and are expensive.

Natural gas consists primarily of methane and some impurities like other hydrocarbons, nitrogen, water vapor,
carbon dioxide and sulphur derivatives. The nitrogen content as well as the quantity of other impurities must be kept below a certain level as a consequence of some legal regulations and technical requirements (reduced heating value, highly contaminated combustion gases). In some countries, the maximal nitrogen content should be below 4%, otherwise the natural gas is considered to be useless in its original state and should be purified. In addition, in gas storage tanks, heavier N₂ molecules settle to the bottom part of the reservoir, increasing nitrogen content to a high level if the gas is taken from these parts of the installation. More than 10% of natural gas resources are considered as sub-par quality due to the high nitrogen content. Several enrichment methods can be applied and are under continuous development: cryogenic distillation (high cost), membrane separation and pressure swing adsorption (PSA) for natural gas purification/enrichment.

The search for new efficient and inexpensive adsorbents is currently an important trend. Such an adsorbent should be capable of exploiting the very small kinetic diameter difference between methane and nitrogen molecules. Among practically applied porous solids, active carbons play a particularly important role since their pore structure can cover different ranges (micropores and mesopores) which enables different applications [15]. In some cases, pore size distribution functions (PSD) are very narrow and pores of uniform size almost exclusively contribute to the total pore volume. Such materials are usually denoted as carbon molecular sieves CMS [16]. As a matter of fact, the narrowness of the PSD function is often an arbitrary parameter, since some carbon materials which claim to be CMS in fact contain rather differentiated pores (of considerable volume) with linear dimensions scattered over a wide range. Some authors [17,18] have shown that the formation of nearly perfect CMS (strictly monoporous) is a primary stage during carbonization of lignin-cellulose materials (wood of different types), provided the process is short (ca. 1 h) and run at moderate temperatures (600–700°C). Carbonization of the same raw material under more severe conditions (extended time, elevated temperature) causes a collapse of the CMS-type structure [19].

Contemporary environmental protection insists on the preservation of natural (green) resources such as trees and forests. This makes all wood-based active carbon (including CMS) fabrication technologies more and more controversial. Regarding this fact, several authors have proposed employing renewable hard wood resources i.e., the dried wood of Salix viminalis [20]. Salix viminalis belongs to the group of short rotation woody crops (SRWC) [21] which are agriculturally cultivated and then harvested as a renewable “green” fuel. Salix viminalis offers a high yield up to 40 tons per hectare/year which is achievable with moderate care and chemical protection [22].

The main aim of the current research involves the practical demonstration of the applicability of Salix viminalis – originated CMSs to the separation of binary gas mixtures.

2 Experimental Procedure

CMS were fabricated from the dried wood of Salix viminalis. Pieces (ca. 4 x ca. 1 mm) of the wood were at first preliminary carbonised at 600°C for 1 hour. After the raw material was placed in a tubular furnace, the temperature in the furnace was increased by 10°C min⁻¹ until the final temperature was achieved. A constant flow of nitrogen (99.99%) was maintained during the whole procedure: heating to the desired temperature, 1 hour of heating at a constant temperature and cooling to room temperature (approx. 2 hours). Then, some samples underwent a subsequent carbonization for 3 hours at 600°C (symbol SV6163) or 700°C (symbol SV6173). Symbol SV denotes type of raw material (Salix – Salix viminalis) while the first two digits correspond to preliminary carbonization (“6” – temperature: 600°C, “1” – time: 1 hour). The last two digits describe the secondary carbonization in the same way as two first digits. A more severe carbonization at an elevated temperature (800–900°C) and extended time (3–5 hours) was not considered since this always causes a collapse in structural parameters such as total pore volume and total surface area. In light of previous studies [19,20,23] the selected carbonization conditions seemed to be optimal for obtaining (from Salix viminalis wood) carbons of relatively well-developed structure but with a preserved very narrow PSD adequate for effective molecular sieving.

Some of the investigated carbon samples like DSV61Zn were obtained by an activation procedure consisting of the application of the zinc chloride method. In such a case, prior to the described preliminary heat treatment (carbonization), dried raw wood of Salix viminalis was saturated with a concentrated solution of ZnCl₂/ZnCl₂/wood mass ratio of 2:3, followed by preliminary carbonization in a neutral gas atmosphere at 600°C for 1 h). The obtained carbon was subjected to intensive rinsing with hot (80°C) deionized water to dissolve and remove zinc derivatives remaining in the carbon matrix. Eluted zinc salts left empty cavities in the matrix which considerably contributed to the pore structure. Based on the results of our previous research [19], the activation procedure significantly
improved the total pore volume and specific surface area ($S_{\text{BET}}$) with simultaneous conservation of the size of pores and a very narrow PSD function in the sub-nanometre range. In this way, we intended to conserve the CMS-type structure of carbons with simultaneous acceleration of the sieving effect due to a high total pore volume and high BET surface area.

Pore structure and specific surface area were determined by a widely accepted method exploiting the phenomenon of low temperature adsorption of chemically neutral gases like nitrogen [24,25]. Nitrogen adsorption isotherms were recorded at the temperature of liquid nitrogen (-196°C) by means of Micromeritics ASAP 2010 equipment. The standard software provided by the manufacturer of ASAP 2010 was employed for the regression of primary obtained adsorption data (nitrogen adsorption vs. relative partial pressure of the adsorptive).

Two regression models were applied: BET [25] for the calculation of specific surface area and the H-K method (Horvath-Kawazoe; [26]) for the calculation of the pore size distribution [27]. All tested carbon samples were degassed under vacuum ($10^{-3}$ Torr) at an elevated temperature (250°C) for an extended period of time (3 hours) before nitrogen/argon adsorption measurements.

Chromatographic tests were performed using a Shimadzu GC-14B gas chromatograph supplied with a TCD detector kept at a constant temperature of 110°C. The carrier gas (helium) was fed at an intensity of 10, 15, 20, 25, 30, 40 and 50 cm$^3$ min$^{-1}$. The flow rate value was set according to the results of the van Deemter optimization procedure performed prior to the separation tests. The glass chromatographic loop was 2.5 m long and of 2.6 mm in diameter. The separation tests were performed at several temperatures (70, 60, 50, 40 and 30°C) and consisted of recording chromatograms for the injected samples (pure gases, two component mixtures and three component mixtures).

The morphology of the carbon samples was investigated by means of an electron microscope (LEO 1430 VP, Electron Microscopy Ltd.) which was supplied with two detectors for secondary electrons (SE), back scattered electrons (BSE) as well as an EDS/EDX microspectrometer (Quantax 200-XFlash 4010, Bruker Ltd.). Adsorbent structures were investigated by the HRTEM method.

### 3 Results and Discussion

Table 1 presents the elemental composition data of the investigated carbons. The results obtained in this study are typical for carbons obtained via the thermal treatment of wood of different kind. Such carbons are characteristic because of the high content of oxygen (usually 10–20%) and carbon content ranging from 80 to 90%. This means that, besides structural heterogeneity (differing curvature of the surface and high adsorption potential inside pores), chemical heterogeneity occurs. Oxygen is much more electronegative than carbon and negative charges must be present on oxygen atoms located on the surface such as surface oxygen functional groups (typically ether, hydroxyl, carbonyl, lactone, carboxyl and acid anhydride). Furmaniak et al. [28] theoretically investigated the problem of gas adsorption on a heterogeneous carbon surface in terms of gas molecule/atom properties and the concentration of oxygen-containing surface functional groups. These studies proved that both the dipole/quadrupole moment of gas adsorptive molecules and the oxygen-dependent heterogeneity of the carbon adsorbent may dramatically alter the properties of the adsorptive-adsorbent system. Thus, the proposed application of CO$_2$ for the characterization of pore structure seems to be questionable in case of heterogeneous surfaces like the surface of most activated carbons and the application of nitrogen for this purpose is scientifically justified [29].

![Fig. 1](image-url) Fig. 1 presents a microscopic structure of the investigated CMS. The material consisted of randomly oriented and twisted graphene sheets which in some areas were parallel to each other. Such spots are usually considered to be graphite microcrystallites. However, the material in general may be described as amorphous. According to the common point of view, the spaces between fragmented graphene sheets are considered to be slit-like pores typical of carbon-type (partly graphitized) porous materials [30]. The presented microscopic structure of CMS SV6163 did not differ substantially from the structure of other samples.

As mentioned, the current study is the first attempt aiming at practical testing of the sieving properties of the CMS and is partly based on some initial studies [23] which showed that simple carbonisation of dried Salix viminalis wood yields strictly monoporous carbons with a pore structure resembling a perfect molecular sieve. However,
the pore structure estimated by the means of static gas adsorption always relies on some theoretical assumptions (the adsorption model) followed by calculations, and in general may not properly reflect the real structural parameters. Such procedures and the resulting PSD functions do not automatically ensure good separation efficiency of such characterised materials, since separation by porous solids is a complex phenomenon influenced by several factors. Thus, a promising PSD function may allow to treat such a material to be a good candidate for an efficient separation medium only [19,20,23].

The tested gases CH$_4$/N$_2$/Kr are relatively inert and are not permanent dipoles (N$_2$ is a quadrupole). Thus, physical adsorption is expected on carbons in a process which relies on non-specific intermolecular interactions between the adsorptive and the real carbon surface. The latter (besides carbon atoms) contains oxygen and other elements in which electric charges may occur. The considered gas adsorptives, besides the common feature of chemical inactivity, do not differ much in size, but the symmetry differences are more important. Nitrogen is a two-atom molecule with dimensions which depend on the orientation of the N$_2$ molecule i.e. dimensions measured parallel or perpendicular to the nitrogen-nitrogen triple bond. The methane molecule and the krypton atom may be seen as quasi-ideal spheres.

In general, the N$_2$ adsorption leads to a fast qualitative evaluation of adsorbent pore structure and allows for an estimate of the specific surface area. We aimed, at first, at such an estimation as a preliminary step necessary for the efficient selection of candidate adsorbents for testing the real molecular sieving abilities (molecular probing) of these materials.

Fig. 2 presents nitrogen adsorption isotherms recorded for the three CMS under investigation, while Fig. 3 depicts the PSD functions which were calculated based on N$_2$ adsorption data and the Horvath-Kawazoe model. These data allowed us to conclude that all of the investigated samples were strictly monoporous, i.e. nearly all pores that contributed to the total surface area/pore volume were of very similar size. The linear dimension of the pores was definitely less than 1 nm. This makes these carbons potential candidates for molecular sieving of gas mixtures, since the average pore size is comparable with the dimensions of gas molecules (Table 2). Frequently, the application of N$_2$ for exact pore structure determination is regarded as questionable due to the proven slow migration of adsorbed nitrogen molecules into (or out of) pores at a temperature of -196°C. Therefore, other test gases have been suggested such as argon and CO$_2$ [28, 29] instead of N$_2$ for pore structure characterisation. However, we have found in the recent literature studies [28] which claim that, in the case of carbons of high oxygen content, PSD functions obtained from N$_2$ and Ar adsorption are rather similar, while the application of CO$_2$ is rather questionable. Our low temperature N$_2$ adsorption results led us to consider the three tested types of carbon as promising
candidates for dynamic sieving of a CH<sub>4</sub>/N<sub>2</sub> binary mixture (supplementary studies on CH<sub>4</sub>/Kr and Kr/N<sub>2</sub> mixtures).

As mentioned, the pore structure of the obtained *Salix viminalis*–derived carbons was dominated by ultra-fine pores of sub-nanometre size comparable to the size of atoms and molecules. The literature quotes similar kinetic diameters for nitrogen and methane (N<sub>2</sub> – 0.364 nm and CH<sub>4</sub> – 0.360 nm, Table 2), but some resources suggest a different diameter for N<sub>2</sub> molecules, depending on the molecule’s orientation, i.e. if measured perpendicular to the N-N bond, the dimension is much smaller (0.300 nm). After the CH<sub>4</sub>/N<sub>2</sub> mixture (1:1 volume) was injected into a chromatographic column packed with the investigated CMS materials, the retention times were measured. Table 3 presents the chromatographic data recalculated to determine the separation factors. The retention times for CH<sub>4</sub> were, in general, very long (8–50 minutes) at all investigated temperatures (30–70°C) and on average were 3–4 times longer than for nitrogen (for a particular adsorbent). This ensured very good separation of the chromatographic peaks (Fig. 4). The calculated separation factors for the CH<sub>4</sub>/N<sub>2</sub> mixture were spectacularly high for all of the investigated samples: 3.64–4.14 (SV6173), 4.80–5.87 (SV 6163) and 7.36–10.20 (DSV61Zn). The lower values of the separation factors correspond to the relatively high temperature of 70°C while the higher values correspond to 30°C. These results suggest rapid and easy desorption of nitrogen (and weak adsorption) and slow desorption (and more durable adsorption) of methane. Separation could be even better at temperatures below 30°C. However, at lower temperatures the separation process had to take more time. The separation time if extended may not be acceptable in real industrial conditions. Thus, a compromise must be found between separation effectiveness and duration.

The experiments were performed in chromatographic conditions while real industrial separation proceeds in PSA installations. However, the chromatographically determined high separation factors are very promising for the application in an industrial scale.

In our study, krypton served as the reference gas since it is comprised of atoms which are very similar in size and shape to CH<sub>4</sub>, which are the molecules to be separated from N<sub>2</sub> molecules as the main task of the study. The retention times for krypton are practically equal to the retention times for methane. Also, Kr atoms are retained, on average, 3-4 times longer than N<sub>2</sub> in the columns filled with the investigated nano-structured CMS materials. The shorter retention times for N<sub>2</sub> are influenced by several factors, but the non-spherical shape of an N<sub>2</sub> molecule and its reduced dimension if measured perpendicular to the N-N triple bond play a crucial role. The separation factors in Table 2 are much more promising than ones determined for other adsorbents of potential industrial importance like silicate [30].

Extensive studies [6,31,32] on the mechanism of adsorption on CMS have led to the conclusion that two basic factors are essential for the overall process: Factor (1) - entering the pore and passage through the pore neck (repellent potential barrier at the pore entrance) and Factor (2) - diffusion along the pore walls (spot-to-spot transfer of molecules). In many cases, the adsorption/desorption rate and velocity are limited by the entry through the pore aperture, which may be considered as a “geometric
factor which is in fact an interaction with the repellent potential barrier at the entrance. Some authors state that, for molecular sieves, diffusion through pore entry is adsorption/desorption rate-limiting, and the order of the adsorption activation energy $E_{\text{ADS}}$ is strongly influenced by the atomic/molecular size of adsorbate. Successful passage through pore entry (in both directions: adsorption-desorption) is a key factor in molecule discrimination by shape as suggested and proven in several studies [6,32,33,34,35].

During chromatographic separation, each molecule/atom of the gas phase repeatedly undergoes an adsorption/desorption cycle in subsequently changing pores as the gas phase components pass through the column. In a chromatographic column, gases get split at the beginning part of it, then move separately along the column and individually undergo adsorption/desorption cycles (in contrast to parallel adsorption/desorption in PSA). The above statements led us to conclude that the kinetics of adsorption/desorption plays a crucial role in the determination of retention time for particular gas mixture components under separation.

Corrected retention times ($t_R$) allow for calculating its dependence on the inverse of temperature ($1/T$). The slope of line dependences: $\ln t_R = f(1/T)$ is in direct relation with the isosteric heat of adsorption ($Q_{ST}$). $Q_{ST}$ directly influences a crucial elemental process in gas chromatography, i.e. the adsorption and desorption of gases, since the activation energy of desorption $E_{\text{DES}} = Q_{ST} + E_{\text{ADS}}$ ($E_{\text{ADS}}$ – activation energy of adsorption). $E_{\text{ADS}}$ (according to the dual barrier model) depends on the energy necessary to overcome the repellent potential barrier at the pore entry $E_{\text{ENT}}$ and the activation energy of diffusion process in pores $E_{\text{DIF}}$ (diffusion of atoms/molecules in pores is an activated process and $E_{\text{DIF}}$ is the energy necessary to enable activated diffusion in pores). Thus, $E_{\text{S}}$ is influenced by the pore entry potential barrier $E_{\text{ENT}}$ and $E_{\text{DIF}}$ i.e. $E_{\text{ADS}} = f(E_{\text{ENT}}, E_{\text{DIF}})$ where $E_{\text{ENT}}$ is strongly dependent on the atomic/molecular size of adsorbing gases/vapours (is higher for bigger atoms/molecules). The separation of gases in chromatographic conditions is a dynamic process directly related on the adsorption/desorption kinetics. The rate of adsorption $V_{\text{ADS}}$ is proportional to $\exp(-E_{\text{ADS}}/RT)$ while the rate of desorption $V_{\text{DES}}$ is proportional to $\exp(-E_{\text{DES}}/RT)$.

Table 3: Separation factors for investigated binary mixtures.

| Carbon SV6173 [312 ± 9.5 m² g⁻¹] | CH₄ + N₂ | Kr + N₂ | CH₄ + Kr |
|---------------------------------|---------|---------|---------|
| CH₄ + N₂                         |         |         |         |
| Temp [°C]                        | $R_s$   | $\pm \Delta R_s$ | $R_s$   | $\pm \Delta R_s$ | $R_s$ | $\pm \Delta R_s$ |
| 70                              | 3.64    | 0.31    | 3.59    | 0.26    | 0.20    | 0.06    |
| 60                              | 3.55    | 0.24    | 3.70    | 0.16    | 0.20    | 0.10    |
| 50                              | 3.74    | 0.62    | 3.81    | 0.21    | 0.17    | 0.07    |
| 40                              | 3.83    | 0.53    | 3.91    | 0.15    | 0.15    | 0.07    |
| 30                              | 4.17    | 0.34    | 4.65    | 0.73    | 0.33    | 0.37    |

| Carbon SV6163 [358 ± 10.94 m² g⁻¹] | CH₄ + N₂ | Kr + N₂ | CH₄ + Kr |
|---------------------------------|---------|---------|---------|
| CH₄ + N₂                         |         |         |         |
| Temp [°C]                        | $R_s$   | $\pm \Delta R_s$ | $R_s$   | $\pm \Delta R_s$ | $R_s$ | $\pm \Delta R_s$ |
| 70                              | 4.80    | 0.75    | 4.90    | 0.34    | 0.41    | 0.26    |
| 60                              | 4.71    | 0.26    | 4.88    | 0.23    | 0.31    | 0.10    |
| 50                              | 4.91    | 0.19    | 5.04    | 0.73    | 0.34    | 0.19    |
| 40                              | 5.25    | 3.52    | 4.91    | 0.67    | 0.31    | 0.39    |
| 30                              | 5.87    | 0.01    | 6.23    | 1.60    | 0.28    | 0.28    |

| Carbon DSV61Zn [1263 ± 50 m² g⁻¹] | CH₄ + N₂ | Kr + N₂ | CH₄ + Kr |
|---------------------------------|---------|---------|---------|
| CH₄ + N₂                         |         |         |         |
| Temp [°C]                        | $R_s$   | $\pm \Delta R_s$ | $R_s$   | $\pm \Delta R_s$ | $R_s$ | $\pm \Delta R_s$ |
| 70                              | 7.36    | 0.56    | 7.91    | 0.68    | 0.29    | 0.31    |
| 60                              | 8.53    | 1.79    | 9.00    | 0.84    | 0.48    | 0.40    |
| 50                              | 8.50    | 0.38    | 9.23    | 2.61    | 0.90    | 0.65    |
| 40                              | 9.28    | 0.85    | 10.56   | 1.26    | 0.75    | 0.59    |
| 30                              | 10.20   | 1.12    | 10.78   | 0.99    | 0.56    | 0.24    |

Values for $Q_{ST}$ available in the literature for N₂, CH₄ and Kr for various carbon-type adsorbents are quite different. However, in many cases, the values fulfil the relation $Q_{ST}$ (N₂) < $Q_{ST}$ (CH₄) = $Q_{ST}$ (Kr). This situation corresponds well
with our studies (Table 4). This explains the essentially equal retention times for Kr and CH₄, in which case all factors influencing E_ads and E_des (the size of molecules/atoms and QST values) are practically identical.

The differences between (QST determination) the studies known from literature are the result of the differing chemical composition of carbons, different measurement conditions (temperature range and surface coverage) and experimental methods (calculations based on adsorption isotherms or calorimetric determination). Thus, any comparison of QST values for the three gases should involve only cases when all gases are investigated in one study over one selected carbon-type adsorbent. Usually, as in our study, QST values for nitrogen are much smaller than for CH₄ and Kr (on carbon-type adsorbents) which effect prefers a faster desorption of N₂. Even when QST values were comparable (22.8 kJ mol⁻¹ for Kr and 23.9 kJ mol⁻¹ for N₂), the adsorption/desorption of N₂ was much faster for these smaller molecules [6].

The pore entry potential barrier is minimal along the pore centreline of slit-shaped pores (typical for carbons) and the pore entry potential barrier is much lower along the pore entry. The gas split depended on the molecular/atomic size of the adsorbate and QST values which were very similar for Kr and CH₄ but much different for N₂. Therefore, separation of N₂ was easy at all the investigated temperatures, but it was not possible to split the Kr/CH₄ mixture by means of the carbons under investigation.

|    | QST [kJ mol⁻¹] |
|----|---------------|
| Kr | 15.02         |
| CH₄| 14.40         |
| N₂ | 7.87          |

4 Conclusions

These investigations have shown that the separation of binary mixtures of CH₄/N₂ and Kr/N₂ does not differ regarding either retention times or separation factors (for a particular packing of a column) for all three investigated CMS. Despite the substantial differences in pore structure parameters such as S_ads and V_ads for SV6163 (and SV6173) versus DSV61Zn, all carbons separated CH₄/N₂ and Kr/N₂ mixtures with the same efficiency. This was attributed to the practically identical i.e., very narrow range of PSD function for DSV and SV carbons despite differences in the preparation methods. Also, the elemental composition for both carbons was comparable, which affected the transport of atoms/molecules along the pores after passage through the pore aperture. The gas split dependent on the molecular/atomic size of the adsorbate and QST values which were very similar for Kr and CH₄ but much different for N₂. Therefore, separation of N₂ was easy at all the investigated temperatures, but it was not possible to split the Kr/CH₄ mixture by means of the carbons under investigation.

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