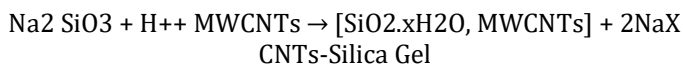
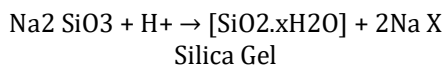


**Figure 1:** The AFM images of MWCNT-Silica gel gas chromatography adsorbent.



In next step, for making suitable mesh, spraying the solution with high pressure into the hot oil was done by oil drop method. Washing MWCNT- SiO<sub>2</sub> mixture by water and organic solvents was the next step for removing oil and other impurities. Then by blowing warm air, solvent was evaporated. Fixing of mixture was done by calcination of the mixture at 200°C in oven. Meshing process was the final step (60-80). After that, adsorbent got ready for packing in suitable GC packed column. Figure 1 shows AFM (Atomic force microscopy) image of this new adsorbent. The AFM images were obtained with CSM instrument. For the analysis of samples, firstly sample were speeded in dimethylformamide (0.1 mg/mL) by sonication for at least 1 h, then 5 µL of that was scattered onto a mica sheet and scans were carried out with a scan rate of 1.0 Hz.

pH is the most important factor in gelation time. Based on this factor, pH must be tuned for getting best mesh and highest quality, because an aggregation may takes place and desired mesh cannot be produced after oil drop method (12). The lowest gel forming was occurred at pH=2 and fastest gelation time is at pH=6 (13) and due to importance of homogeneous mixing of solution, pH=2.5-3.5 was selected.

### 3. Result and Discussion

#### 3.1 Separation of linear and branched alkanes by Silica gel adsorbent

In first step of experiments, an unmodified silica gel packed column was employed on Shimadzu and stabilization was achieved after 4 h at 200 °C with a carrier flow rate 50 ml/min. Other instrument conditions were listed at table 1. After that, 1 ml of hydrocarbons mixture, includes equal value of propane, 2-methylpropane, n-butane, 2,2-dimethylpropane, 2-methylbutane and n-pentane were injected

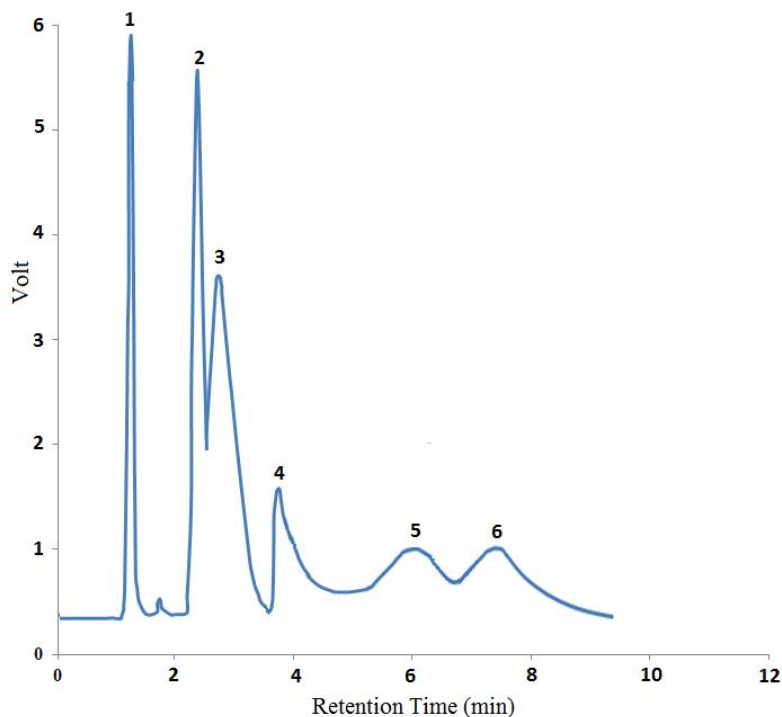
and gas chromatogram of this mixture at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min was obtained (figure 2). As shown in figure 2, based on nature of silica gel and polarity of this adsorbent, elution of all compounds was done after applying temperature program and asymmetric and tailed peaks were obtained. 2-methylpropane and n-butane have same molecular mass and so were co-eluted at close retention time. Except 2,2-dimethylpropane (due to its space shape), two other C5 hydrocarbons (2-methylbutane and n-pentane) were co-eluted at near retention time and their peaks were tailed and silica gel could not apply proper gradient adsorption on this mixture of compounds.

### 3.2 Separation of linear and branched alkanes by modified MWCNT-Silica gel adsorbent

In next step and the same column conditions, ability of modified MWCNT-silica gel adsorbent was tested by injection of hydrocarbons mixture. As shown in figure 3, six incredible symmetric peaks were appeared and hydrocarbons were eluted in longer time and separation at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min was done completely.

There are some reasons for interpretation of this good separation. The first reason is increasing of active surface due to characters of MWCNT. Functional MWCNTs are open-ended tubes and have extended surface in and out of tubes. These holes on surface of adsorbent increase active surface for interaction with analytes and based on Van de Waals forces and entropy, interaction of non-polar molecules are different on surface of adsorbent.

On the other hand, strength of the interaction is related to length of hydrocarbon, surface area and hydrophobicity of surface. This statement is the main reason for separation of linear hydrocarbons. On the other side, branched hydrocarbons are affected by entropy effect and they cannot have strong interaction with surface as well as slender molecules and so, their rate of exit is increased. The second reason for this good sieving is that branched hydrocarbons cannot pass interstices of MWCNT or between of them.



**Figure 2:** Chromatogram collected of a alkanes mixture sample with equal value on unmodified silica gel, at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min. propane (1), 2-methylpropane (2), n-butane (3), 2,2-dimethylpropane (4), 2-methylbutane (5) and n-pentane (6).

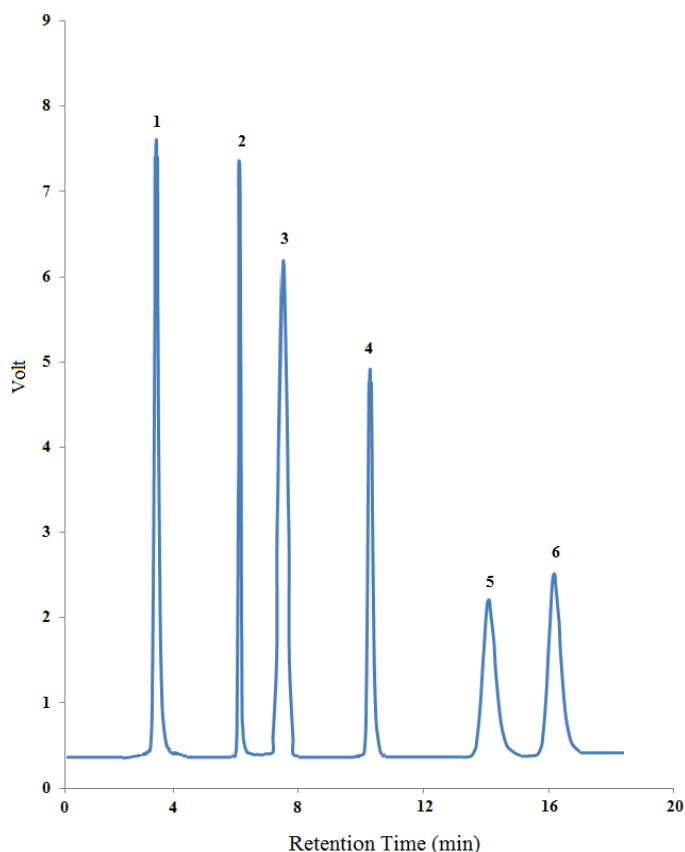
Jiang et al. found out that branched hydrocarbons cannot fit between SWCNT bundles and based on this

effect, a molecular sieving was occurred on surface of adsorbent (14). Last effect is applying of programmed temperature on column. Different molecular shape causes a variety of Wan der Waals interaction between adsorbent and analytes and based on correlation of Wan der Waals interaction and temperature, adsorption and desorption processes were done completely.

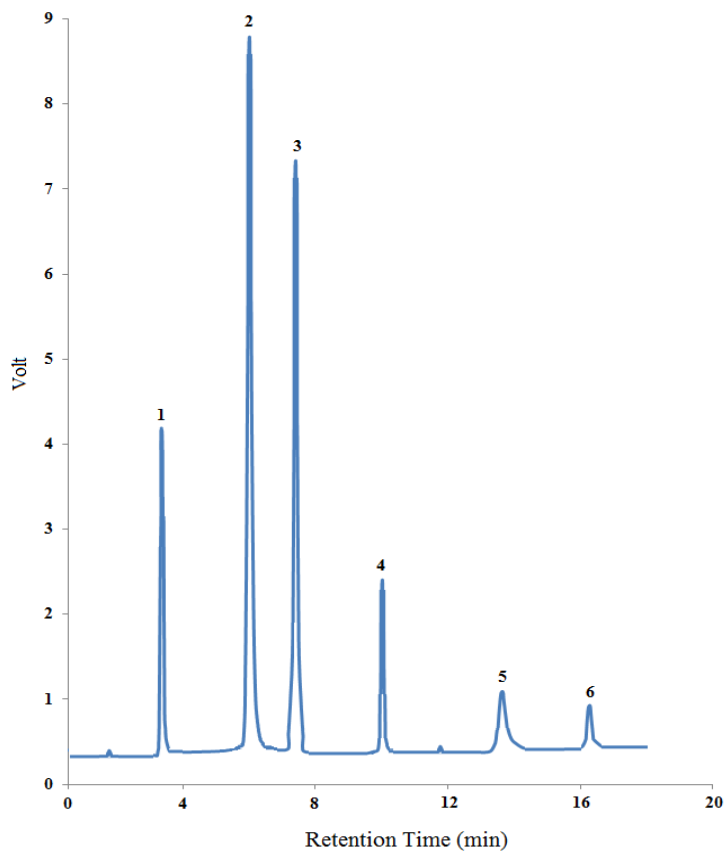
### 3.3 Determination of hydrocarbons in a LPG sample by modified MWCNT-Silica gel adsorbent

Based on column performance on separation of alkanes mixture, a certified LPG sample was injected and figure 4 at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min was obtained. As figure 4 shown, gas chromatogram of LPG shows propane, 2-methylpropane, n-butane, 2,2-dimethylpropane, 2-methylbutane and n-pentane. For quantification of alkanes in LPG, standard addition was used and propane and 2,2-dimethylpropane were selected for standard addition and five different syringes (5  $\mu$ L, 10  $\mu$ L, 25  $\mu$ L, 50  $\mu$ L and 100  $\mu$ L) was used and five point calibration curve for propane and 2,2-dimethylpropane was generated (figure 5 and 6). The linear regression equations and the correlation coefficients (R<sup>2</sup>) for propane and 2,2-dimethylpropane were obtained.

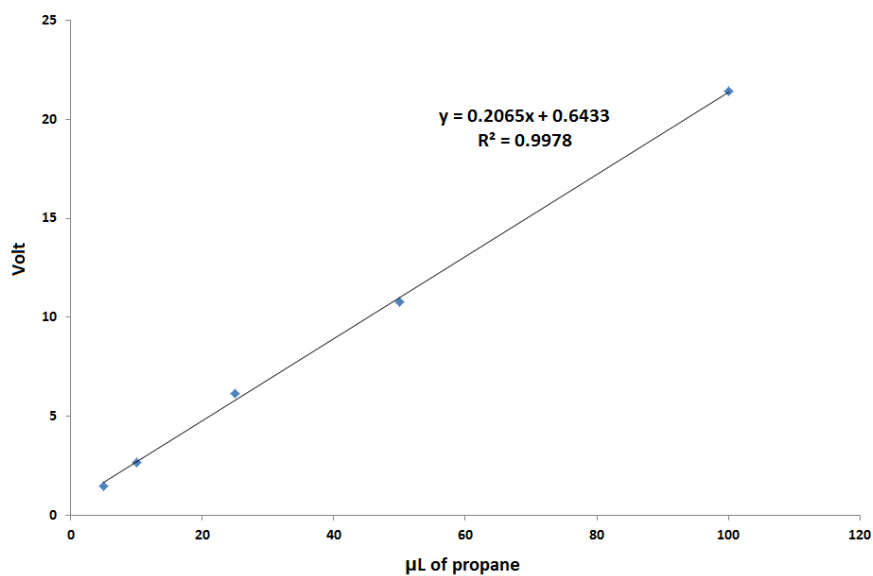
Base on signals and calibration curve, this sample was involved: 33% 2-methylpropane, 30% n-butane, 18% propane, 10% 2,2-dimethylpropane, 5% 2-methylbutane, 3% n-pentane and 1% other compounds. RSD% is from 8 to 13% for determinations.



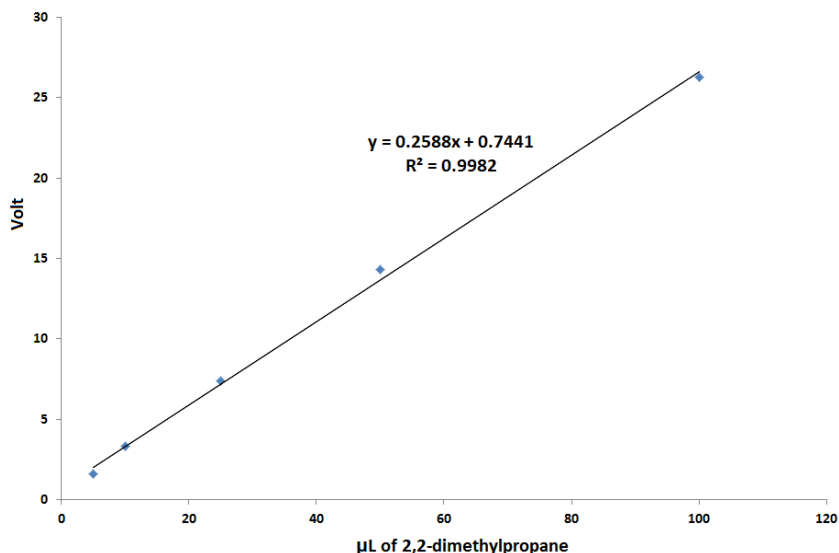
**Figure 3:** Chromatogram collected of a alkanes mixture sample with equal value on MWCNT-Silica gel, at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min. propane (1), 2-methylpropane (2), n-butane (3), 2,2-dimethylpropane (4), 2-methylbutane (5) and n-pentane (6).



**Figure 4:** Gas chromatogram of LPG sample on MWCNT-Silica gel adsorbent at column temperature program from 180 to 220 °C at 5 °C/min and carrier flow rate 35 ml/min. propane (1), 2-methylpropane (2), n-butane (3), 2,2-dimethylpropane (4), 2-methylbutane (5), n-pentane (6).



**Figure 5:** five point calibration curve of standard addition for propane (5 µL, 10 µL, 25 µL, 50 µL and 100 µL).



**Figure 6:** five point calibration curve of standard addition for 2,2-dimethylpropane (5 µL, 10 µL, 25 µL, 50 µL and 100 µL).

#### 4 Conclusions

In this study, a new silica gel based adsorbent was fabricated and its ability in separation and quantification of alkanes mixture was investigated. Compared with silica gel adsorbent, MWCNT-silica gel shows some advantages: (1) more surface area and therefore more symmetric peaks, (2) more retention time that cause increase sensitivity and separation ability for mixtures with near boiling points and (3) ability for separation of polar and nonpolar mixture in one injection.

#### 5 Acknowledgements

Support of this work by grants of the Research Institute of Petroleum industry (RIPI) and K. N. Toosi University of Technology for doing experiments is gratefully acknowledged.

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