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APPLICATION OF HYDROGELS IN DRYING OPERATION

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Abstract
The purpose of this work is investigation of hydrogels as a humidity absorbents for drying of natural gas and oil products ex. gasoline and kerosene.
In industries, absorption operation selection is related to absorption capacity of solids and its recoverability.
In this work, one type of hydrogels with the commercial name A-100 and particle diameter 35<mesh<60 (micron) has been investigated. This type of hydrogel, is one of the strong absorbents. In this study, absorbent recoverability, the amount of humidity absorption and absorption kinetic have been considered.

Key words: drying, hydrogel, absorbent, oil product, absorption kinetic, absorbent recoverability

1. Introduction

In absorption operation, the components of gas or liquid solution can be separated. gas and liquid absorption operations are similar, because in all of these, solution that should be separated, is contacted with other insoluble phase (the same of solid absorption) and un-equal distribution of initial materials between absorbed phase in solids and fluid bulk is the reason of separation.
Absorption operations are physically or chemically. whereas, chemically absorption or activated adsorption, is the result of chemical reactions between solids and absorbed materials.
Absorbed solids are granularly with diameter of 50 micron to 12 millimeter, generally. Solids, due to its application and using case, should have some of operating:

- Absorbents in fixed beds with gas or liquid flows, shouldn't caused high pressure drop.
- Absorbents shouldn't transferred with fluid flow.
- Absorbents should have a good resistance against crushing due to transportation and the weight of absorbents.
- The absorbents, while transportation, should flow from storage vessels, easily.
- The absorbents should have high absorption ability.
- The absorbents should have a large surface area.
- The absorbents, should be recoverable for repeated operation.

The main absorbents with general using are:

1. Fuller's Earths
2. Activated clays
3. Bauxite
4. Alumina
5. Bone char
6. Decolorizing carbons
7. Gas-absorbent carbon
8. Molecular-screening activated carbon
9. Synthetic polymeric adsorbents
10. Silicagel
11. Molecular sieves

2. Polymers can be easily convert to gel form

Hydrogels are polymeric networks that have ability for absorption a large amount of aqueous solutions. The water absorption ability of these materials, is related to groups on the main polymer chain, whereas, it's resistance against dissolving, is due to cross grafts between polymeric chains.

3. Hydrogel Construction

Three dimensional jetty can be the best incarnation of a hydrogel construction, that is include linear chains of polymers with covalence connection, connected together by cross connections (according to figure 1-1).

Cross connections can be covalence, ionic grafts or crystal sections. There are polar groups at the distances between cross connections on the polymer chains. Hydrogel is due to polarity and hydrofill groups on the chain and insolubility of hydrogel is due to cross connections.

4. Hydrogel preparation procedure

The synthesis of hydrogels in industry is Consist of solution and reversed suspension and reversed emulsion polymerizations.

Figure 1 shows a block diagram of a generic solution polymerization process. This figure, represents the major procedure of super absorbent polymer manufacturing in the laboratory and industrial scales.

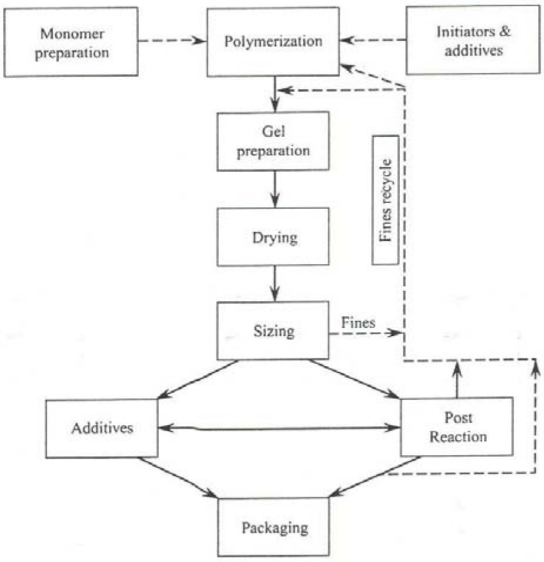
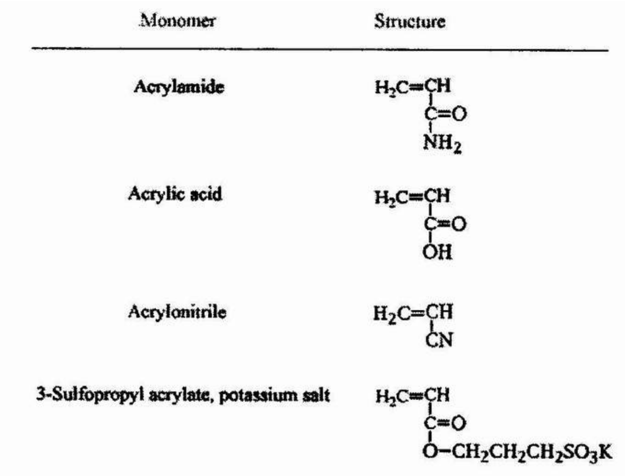


Figure 1. hydrogel preparation block diagram (solution polymerization procedure)

5. Experiment & Tests

Figure 2 represents numbers of monomers using in preparation and construction of hydrogels.



Monomer	Structure
Acrylamide	$H_2C{=}CH{-}C({=}O){-}NH_2$
Acrylic acid	$H_2C{=}CH{-}C({=}O){-}OH$
Acrylonitrile	$H_2C{=}CH{-}CN$
3-Sulfopropyl acrylate, potassium salt	$H_2C{=}CH{-}C({=}O){-}O{-}CH_2CH_2CH_2SO_3K$

Figure 2. samples of used monomers in preparation of hydrogels.

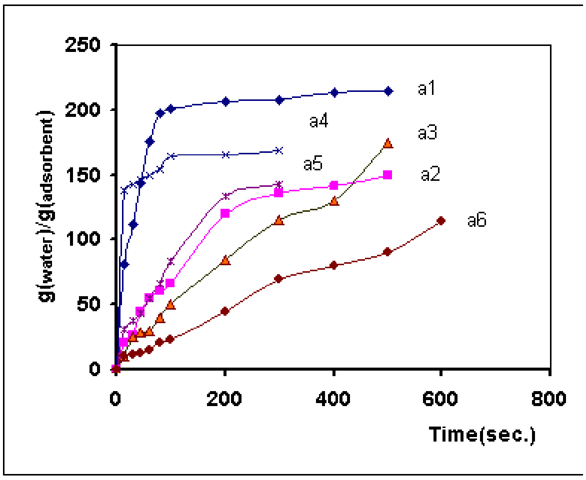


Figure 3. a1: A-100, a2 : H-100, a3 : sap composite, a4 : A-200 (mesh<60), a5 : A-200 (18<mesh<60), a6 : A-200 (mesh<18).

In this study, at first, the absorption kinetic of prepared hydrogel sample has obtained (according to figure 3).

As shown in figure 3, A-100 hydrogel with particle size (35<mesh<60 micron) has been selected for next tests.

The complementary tests are include (a) determination the amount of absorbed water by hydrogel with gel formation and also, final capacity of gel for water absorption (until saturation), (b) determination the rate of absorbent inflation in an oil feed, and (c) considering the operation recoverability (ability of absorbent for regeneration and reusing).

5.1. Hydrogel Capacity

In absorption process laboratory studies, the main aim is determination of hydrogel absorbent capacity and the amount of absorbed water by hydrogel until uniform gel formation. The necessary tests for absorption operations have been done in two independent water and vapor phases. The test results are given in table 1 and 2, respectively.

Table 1. Test result in water phase

Sample state	Absorbed water volume (ml)	Time (sec.)
Inflated with uniform gel formation	70.5	150
Final inflation (saturated of absorbed water)	198	545

Table 2. Test result in vapor phase

Sample state	Absorbed water volume (ml)	Time (min.)
Inflated with uniform gel formation	68	69

5.2. Inflatable Hydrogel

There is a general relation between polymer inflation, solution and polymer state. Inflation percent (or mass inflation) is the major parameter in the hydrogel inflation studies. Inflation percent (%S) is calculated this equation:

$$\%S = \frac{m_t - m_\circ}{m_\circ} \times 100 \qquad (1)$$

The isotherm curve of A-100 hydrogel inflation ability has been show in figure 3.

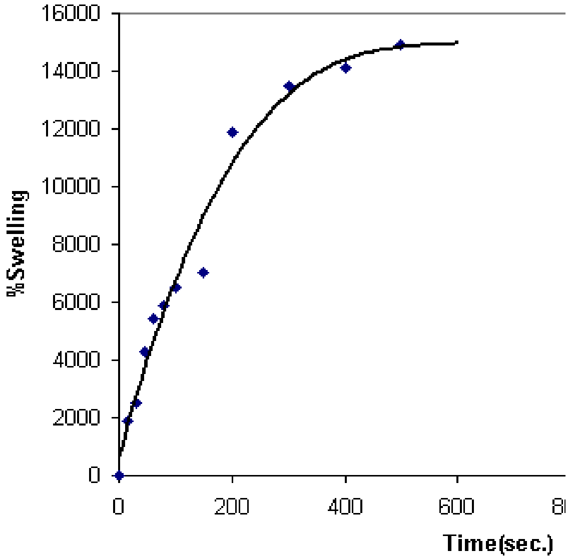


Figure 3. Isotherm curve A-100 hydrogen inflation ability

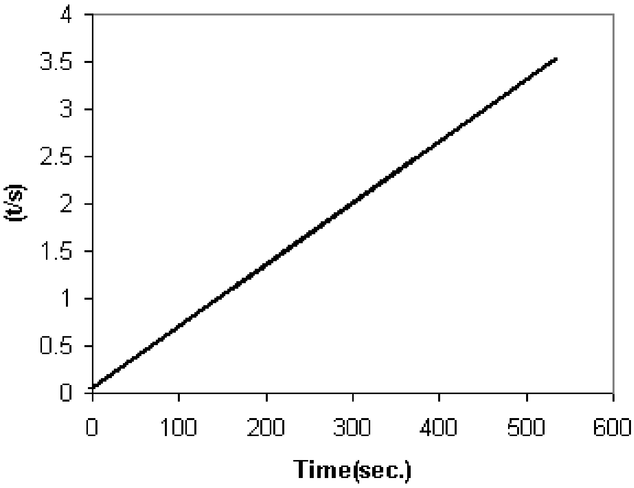


Figure 4. Hydrogen inflation rate curve

5.3. Equilibrium Water Content (EWC)

The quantity of absorbed water by hydrogel is determined by using EWC relationship. This relation is give as :

$$EWC = \frac{m_S - m_\circ}{m_S} \qquad (2)$$

The range of EWC for A-100 hydrogel is about between 0-995.

6. Inflation Kinetic Studies

Inflation kinetic of high inflatable polymers is second order and represented according to following relation:

$$\frac{t}{S} = A + Bt \qquad (3)$$

Figure 4 presents linear regression of inflation curve according to relation 3 for A-100 hydrogel.
Initial inflation rate, inflation rate constant and theory amount of equilibrium inflation for aforesaid hydrogel is calculated from slope and initial value of presented curve in figure 4, respectively.
These results gives in table 3.

Table 3. A-100 hydrogel inflation rate parameters

Initial inflation rate $(ds/dt)_0$, $G_{watre}/g_{absorbent}$ min	**Inflation rate constant g_{gel}/g_{watre} min ,** $K_S \times 10^6$	**Theoretical equilibrium inflation S_{max} , $g_{water}/g_{absorbent}$**
65	0.2556	19700

6.1. Inflation kinetic order

When a glassy hydrogel is contacted with water, water molecules influence to hydrogel and inflate it. Said influence is caused spaces between hydrogel chains, dynamically.
large scale Hydrogel inflation, is caused polymeric sections movement and finally distance increasing between hydrogel chains. In recent years, the influence analysis of water to inflatable polymeric systems, because important applications of these polymers in biomedical, medical, Environmental Engineering and agriculture, have considered, more than ever.
Inflation mechanism of hydrogels is determined using following correlation :

$$F_{SWP} = \frac{m_T - m_\circ}{m_\circ} = kt^n \qquad (4)$$

according to Fick's influence theory and for cylindrical forms "n" is between 0.45-0.5, whereas , 0.5<n<1 indicates non Fick's influence. The curve of ln(F_{SWP}) against ln(t) using inflation kinetic for A-100 hydrogel has been drawn in figure 5.
Inflation order (n) is calculated from curve slope. From existing curve in figure 5, n=0.885 and so, influence type of hydrogel system don't observe from Fick's theory.
Meanwhile, studies until this stage are practicable for all of hydrogel samples.

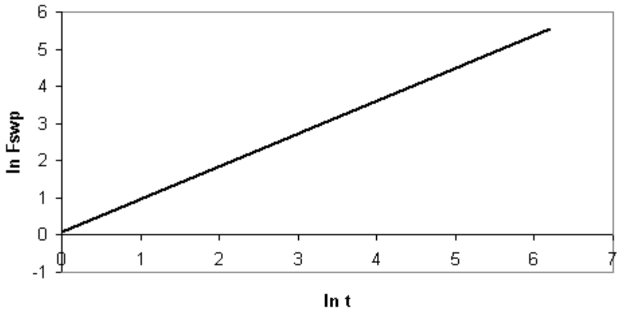


Figure 5. A-100 hydrogel inflation kinetic curve

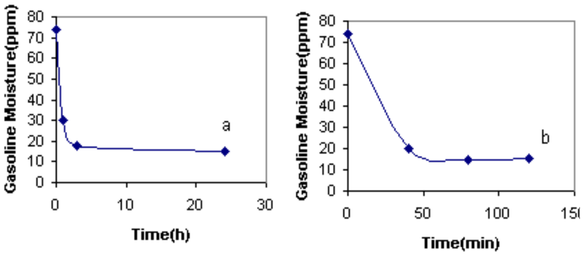


Figure 6. isotherm curves of A-100 hydrogel inflation in oil samples fixed state , (b) mobile state

6.2. Absorbent Inflation Rate in an oil sample

For determination the inflation rate of A-100 hydrogel in an oil sample have been used from gasoline of 74 ppm humidity. Related tests have been done in two fixed and mobile independent systems.

In two systems, the procedure of A-100 hydrogel sample floating in solution at ambient temperature and pressure have been used and with measurement the amount of existing humidity in sample at different times, isothermic curves have been obtained.

But, because in floating procedure, the volume change isn't considerable, for measuring the amount of existing humidity in sample have been used from ASTM D-1533 standard, that is a standard procedure for measurement the existing water in liquid using heated fisher's calometric titration.

Inflation isotherm curve for two fixed & mobile state are according to figure 6.

7. Hydrogel Regeneration (Repeatability)

Absorbent recoverability for reusing is very important, industrially. In this study, repeated wetting - drying of hydrogel sample have been done. Drying test and repeated wetting-drying cycle with preparation of uniform gel is done with 1.0 gram of A-100 hydrogel and 70.5 ml water. In this test, drying have been studied in two independent procedures (1) hydrogel regeneration using acetone washing (or low molecular weight alcohols and ketones) and (2) drying in heated even.

Industrially, after gel preparation, the water content of hydrogel is reduced until 1 to 5 weight percent using evaporation and conductive heating.

Generally, using of two dryer types is custom. This section includes (a) through circulating belt, and (b) rotating drum.

The results of hydrogel regeneration by acetone washing and heated oven at 90^{o}C are presented in tables 4 and 5 , respectively.

Table 4. Test results of hydrogel regeneration with acetone in any cycle

	1st cycle	2nd cycle	3th cycle
Hydrogel weight (gr)	0.7725	0.5747	0.4488
Absorbed water until uniform gel formation(ml)	62.5	57.2	53

Table 5. Test results of hydrogel drying with heated oven at 90^{0}C in any cycle

	1st cycle	2nd cycle	3th cycle
Hydrogel weight (gr)	1	1	1
Absorbed water until uniform gel formation(ml)	68.4	59.2	53.8

Meanwhile, after any drying cycle, particles resizing will be necessary. After drying operation, hydrogel particles hang together and then, aforesaid hydrogel isn't applicable and must be resized. In industry, usually, sizing process according to figure 7 is used.

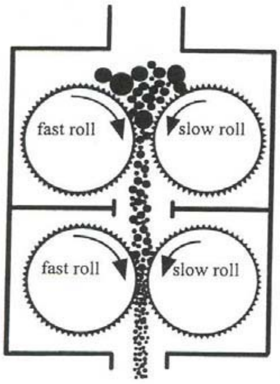


Figure 7. Schematic diagram of a two-pair high roll crusher

8. Results and Discussion

When humidity content of liquid product is little or about ppm, hydrogels are comparable with other absorbents, ex, silicageles. Especially, for tested sample in this study that has desired absorption capacity and rate. But obtained results from tests represent studied hydrogel comparison with other absorbents has low facing for drying of oil samples.

The reasons are caused to alteration of hydrogel role for oil product drying are:

- After gel formation, transportation and transferring of it from a vessel to another vessel is difficult.
- Hydrogels drying or regeneration using ketones washing, requires a large volume of washing solution that may not be economically.
- Hydrogel regeneration using acetone washing is caused to stick hydrogel pieces to vessel wall.
- Drying using oven at temperatures below 100°C very long time, but, high temperatures aren't recommended.
- Repeated drying by oven is caused sample absorption ability reducing.
- After drying, for their excess equipments are required for hydrogel resizing.

If the weak points of hydrogel related to repeatability for absorbent regeneration and reusing are removed, it may be possible that hydrogel can be an efficient absorbent for oil products drying in feature.

Nomenclature

$A = \frac{1}{K_S . S_{eq.}{}^2}$: Initial hydrogel reversed rate

$B = \frac{1}{S_{eq.}}$: Inflation maximum

K : Inflation constant

K_S : Inflation rate constant

m_o : Dry hydrogel mass (g)

m_s : Inflated hydrogel mass at equilibrium time (g)

m_t : Inflated hydrogel mass at time t (g)

n : Inflation order

S : Inflation amount at time t

$\%S$: Inflation percent (%)

t : Time

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