

Short-Review Article

Investigation of Hydrate Formation Kinetics and Mechanism of Effect of Inhibitors on it, a Review

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Abstract: Gaseous hydrates are ice-like compounds of water and gas that are usually formed at high pressures and low temperatures in such a way that in each of their constituent units a gas molecule is enclosed in a cage of water molecules. Gas hydrate was introduced by Hamrasmith in 1934 as one of the problems of the gas industry in transmission pipelines because by reducing the internal cross section of the pipe, it increases the pressure drop and sometimes may lead to complete blockage of the pipe. Hydrate formation can also lead to the destruction of tools in the process including, the valves and sensors, or accumulate in storage tanks, increasing labor costs for cleaning. In industry, one of the thermal, mechanical, thermodynamic and kinetic methods is usually used to prevent or eliminate the formation of hydrate. Thermal methods try to keep the gas away from the formation of hydrates by insulating the pipe, using rotating water or hot oil, or by electrically heating the pipe. The use of pigs is a mechanical method to remove the clogged tubes due to hydrate formation. It is also possible to change the gas mixture by adding a third material to the fuzzy diagram and eliminate the possibility of hydrate formation at the temperature and operating pressure of the system. Kinetic methods help to improve the working conditions of the gas transmission system by increasing the latency or by reducing the growth rate or adhesion of the hydrate crystals.

Keywords: Hydrate; Water molecule; Water; Gas; Pressure; Temperature

Graphical Abstract



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Introduction

Today, the positive aspects of hydrate formation have also been considered. The presence of abundant hydrate reservoirs in offshore areas has led

researchers to look at this material as a new source of energy [1-5]. Also, the high capacity of hydrates in gas storage has introduced its use as a new method in natural gas storage and transport. Considering the

above, familiarity with the mechanism of hydrate formation and how inhibitors and accelerators affect it is a great help to select these substances to prevent the formation of hydrates in cases that disrupt the process and also increase the rate of formation in positive applications [6-9].

Kashchev and Firoozabadi [10] stated that it is possible to form hydrate nuclei at the interface between the water and gas (HEN), vessel walls (HEN) and in the liquid phase mass (HON). He then considered the formation of nuclei at the interface between the water and gas as well as in the walls of the vessel to be more probable due to the less energy required for heterogeneous nucleation. In this research study, it was assumed that the primary nuclei are formed at the interface between water and gas [11-15].



Figure 1. Formation and growth of hydrate crystals at the common water and gas surface

Long and Kwami have proposed a model for hydrate formation. In this model, it is assumed that initially gas molecules penetrate the water-gas contact surface

at the rate $10^{22} \frac{\text{molecule}}{\text{cm}^2 \cdot \text{sec}}$ at temperature and pressure of hydrate formation from the gas mass. Then, due to the catarrhal motions of gas molecules, some of them collide with the water-gas interface and are absorbed on the surface [16-20].

According to the model proposed by Rahman and Stiling, there are cavities in the water surface

composed of water molecules, some of which are not yet stable. In the third stage, the adsorbed gas molecules move on the surface to reach one of these holes. The placement of the gas molecule inside these cavities causes a new balance between its molecular forces to prevail and a complete cavity is formed and begins to grow [21-25]. Therefore, there will be three steps to hydrate formation:

1. Infiltration of gas to the water surface
2. Superficial migration and formation of primary nuclei
3. Growth of crystals

Due to the similarity of the above steps with the crystallization process, many researchers have proposed a kinetic model for the growth of hydrate crystals [26-30].

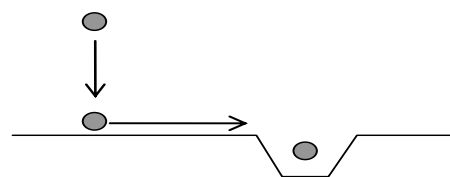


Figure 2. Driving force

The degree of inclination from the state of equilibrium of the driving force is suitable for the performing processes. To model the hydrate production, one must first determine the appropriate driving force for this process. Some researchers have considered the degree of deviation from the equilibrium point B ($P_{exp} - P_{eq}$) or the equivalent of the difference of fugacity's in these two states as the driving force. On the other hand, some articles have considered temperature difference ($T_{exp} - T_{eq}$) as a suitable driving force for hydrate formation and have modeled this process based on it. Knowledge of the following driving force is the difference between liquid mass temperature and surface temperature [31-35].

Introduced Solid Particles

- Basically, the pressure difference as a driving force does not have a correct physical interpretation. This is due to the fact that on the solid surface, the pressure is equal to the equilibrium pressure [36-39].

On the other hand, we know that whenever there is a pressure difference within a liquid system, in a fraction of a second, this pressure difference disappears and the mass pressure becomes uniform. However, more time is needed to create a temperature balance due to the temperature difference [40-45].

- On the other hand, the surface temperature of solid particles should be higher than the temperature of the liquid mass because solid molecules have less energy than the same molecules when dissolved in the liquid phase. Therefore, some heat is released during the hydrate production process, so the surface temperature of the growing particle is higher than the temperature of the inlet mass [46-50].

Various models have been proposed to predict the production of hydrate particles as well as their growth. Kashchev and Firoozabadi have presented the following equation for the rate of crystal production based on the changes in energy required to form hydrates:

$$J = zf^*C_0 \exp\left(-\frac{W^*}{kT}\right)$$

Where J is the particle production rate in terms of particles per cubic meter per second, f * frequency of particle connection to the primary nuclei, z * Zeldovich factor, C0 concentration at the nucleation sites, W * amount of work done to produce the nuclei, T Temperature and k are kinetic constants. He also obtained the following diagrams for nucleation velocities based on different experimental temperatures and pressures.

By presenting the following equation, Chang *et al.* [40] related the growth rate of hydrate crystals in a two-dimensional growth model to the temperature difference relative to equilibrium.

$$r_f = A \times [e^{B(-\Delta g/RT)} - 1]$$

Where r_f is the particle growth rate, A and B are system-related constants obtained by fitting laboratory data, and g is the Gibbs energy change. He then performed the following graph to compare the effect of the driving force.

Historically, studies on the phenomenon of gaseous hydrates can be classified into three important periods:

- The first period, from its discovery in 1810 to the present, is that the hydrate has been studied as an unknown scientific phenomenon in which water and gas are transported into a solid network [51-55].
- The second period, from 1934 until now, has studied the phenomenon of hydrates in the gas transmission industry.
- The third period, from 1960 to the present, began with the discovery of underground hydrate sources in the deep oceans and deep-frozen regions.

In 1778, Joseph Priestley left the window open as he left the laboratory in the winter. When he returned to the laboratory, he noticed that SO₂ vapors had saturated the water and frozen it.

This was not the case for HCl and SiF₄. Priestley was therefore believed to have discovered it thirty years before the hydrate demon was discovered.

The discovery of hydrate by Davy, which was done independently, was considered the first observation of hydrate Becomes.

Sir Davy Humphrey was the first to notice the formation of chlorine hydrate in 1811 during an experiment in cooling a chlorinated aqueous solution to -40°F .

From 1810 to 1934, studies on hydrates were conducted on the following two main axes:

1- Identifying all the compounds that can form hydrates.

2- Quantitative description of compounds in terms of percentage composition and physical properties. [56-59].

From 1934 onwards, research into hydrates led to ways to prevent this phenomenon from occurring in gas transmission lines, because at that time Hammer Schmidt realized that clogged pipelines were due to hydrate formation, not frost. The importance of hydrate has naturally doubled since its discovery in parts of Alaska, Siberia and Canada. These hydrate mineral reserves are known as a pristine source of energy and have been noted for the large amount of gas stored in them.

Methods of Decomposing Hydrates or Preventing Their Formation

Hydrate prevention and decomposition methods are estimated more thermodynamically than the kinetic methods. The main reason for this is the relative difficulty of measuring the time-dependent properties (kinetics) compared with measuring the time-independent properties (thermodynamics). In these processes, the "hydrate formation point" is taken to mean the point at which the hydrate begins to form or the highest possible temperature at which the hydrate can exist (at a given pressure) [60-65].

There are basically 4 ways to break down hydrate or prevent hydrate formation:

1. Separate the water to reduce the gas dew point
2. System temperature control
3. System pressure control
4. Use the inhibitor to transfer the balance

The above methods are used individually or in combination to prevent or rapidly break down hydrates.

Gas hydrate controllers

Hydrate control by separating water (lowering the dew point): The first technique for controlling the hydrates is to isolate the host molecules needed to stabilize the cages. A well-known method that satisfactorily prevents formation of the hydrates in the transmission pipelines is to dehydrate the inlet gas to the pipelines, thereby reducing the dew point temperature to a point where the system does not hydrate at any point. There are two reasons why we should be concerned about the presence of water to form hydrates. The first is that the free water phase is necessary for the formation of hydrates, and the second is that ice is a solid phase that can freeze below temperatures.

NGH (natural gas hydrate) can be composed of gaseous hydrocarbon phase and free water. For example, in the gas pipeline transmission lines, the time it takes for free water to accumulate and be able to form hydrates can take days, months, or even years; Also, a vapor or hydrocarbon liquid containing a small amount of water (less than 1000 ppm) can form hydrates in a certain temperature range (at a constant pressure) without the release of a free water phase. Studies show that if a hydrate nucleus is present (on

the wall), hydrate growth from a hydrocarbon phase occurs easily.

The water entering the process can be completely hydrated and grow to the point where it interrupts the flow. Ice can also form at a constant pressure and in a certain temperature range.

(At temperatures lower than the hydrate formation temperature), which is less important than hydrate formation because it can rarely form. Except for cold conditions, the maximum water content in the gas is

about $4 \frac{\text{Lbm}}{\text{MMSCF}}$ and normally the water

content in the gas is about $2.25 \frac{\text{Lbm}}{\text{MMSCF}}$. After

the free water is separated from the gas flow, two processes are normally used to reduce the dew point by separating the available water. These two processes result from the three types of processes previously proposed in 1946 (dehumidifiers, chemical adsorption by solids, and physical adsorption by solids). It is not economically viable to use non-renewable adsorbent solids [66].

In the first process, the water concentration is reduced by contact of the gas with a compound such as TEG (tri ethylene glycol) (TEG separates water by hydrogen bonding). Calcium chloride is inexpensive and requires little compensation. However, this substance causes corrosion and on the other hand, it lowers the dew point a little and precipitates with hydrogen sulfide. Lithium chloride reduces the dew point by 22-36 °C and is less corrosive, but it is expensive and commercially has impurities that cause corrosion. Di-ethylene glycol does not form in solid concentrated solutions and is stable in the presence of sulfur and carbon dioxide at normal temperatures, but its dew point reduction is less than TEG and its initial cost is high. Tri-ethylene glycol in concentrated

solutions it does not form solids in the presence of sulfur and carbon dioxide at more stable operating temperatures. It is easily and largely recoverable and reduces the dew point to a great extent, but its initial cost is high [67-69].

Tri-ethylene glycol has the best composition in terms of economics and effectiveness. In the second process, the gas contacts a solid such as a molecular sieve (alumina silica gel) that selectively absorbs water. In the first process, TEG, which is a hygroscopic liquid, absorbs water from the gas in an adsorbent with equilibrium isotherm steps, and then the water is given heat to separate the water from the TEG, and then the TEG fluid is recycled to the adsorbent. The hydrogen bonding of water to TEG is so effective that only 2 to 3 equilibrium steps are required and the Overall efficiency of the tray is about 25% to 35% so the adsorbent consists of 8 to 12 trays. The TEG return rate is 2.5-2 LbmTEG per Lbm [70-72].

In the general case, desiccant solids are placed inside two parallel packed beds and gas is passed through those beds. An adsorbent is used to separate water from the gas while the parallel unit is being regenerated (for example at high temperature).

There are several desiccant solids, the most common of which depends on the drying efficiency of the silica gel. Alumina and sieve are molecular. In recent years, molecular wrecking has become more common due to its benefits.

One of its main advantages is that it significantly reduces the dew point and also absorbs a relatively large amount of water compared to the number of hydrocarbons and that it is not damaged by water like silica gel. Molecular sieves are crystalline solids that provide the lowest dew point achievable.

Molecular sieves are designed to absorb specific molecules based on polarity, reducing their selectivity to water, alcohol, glycol, hydrogen sulfide, carbon dioxide, and even mercaptans and heavier organic matter, albeit in small amounts. By mass) absorb. Research results show that methanol injection is superior to both activated alumina for inlet gas with 4 $\text{lbH}_2\text{O}/\text{MMSCF}$ and molecular sieve for inlet gas with 23 $\text{lbH}_2\text{O}/\text{MMSCF}$ in a turbine expansion base. For processes with very low temperatures, such as turbine expanders with discharge temperatures below 160 °F, the usual procedure is to use a molecular sieve.

Controlling Hydration by Heating: When the system contains steam and hydrate in equilibrium, heating can lead the system to the vapor-liquid equilibrium region. Heating may be done at constant pressure in a heat exchanger [73-75].

The sensible inlet heat causes point A of steam and hydrate to point B (LW-H-V equilibrium). At point B, the first drop of water, which is the result of hydrate decomposition, appears. All the input energy is used to decompose the hydrate at a constant temperature and pressure. The more hydrate is broken down, the more gas and liquid it contains. Until the hydrate disappears globally, at this time the perceptible heat causes the vapor and liquid phases to settle. Then the free water phase can be separated using mechanical means.

If free water is converted to hydrate and then this hydrate decomposes but some of its structures remain, the hydrates will re-form. Heating to decompose the hydrate should be done carefully by starting the heating from both ends of the tube. Then extend to the middle of the tube. If a hydrate structure decomposes

from the middle (heating from the middle of the tube), the decomposed hydrates at both ends may increase the pressure exponentially with increasing temperature. High pressures in the pipeline can cause explosions and fires in the walls of the equipment. Heating to break down hydrates should be done with caution as it is not uncommon for pipes to burst [76-79].

One way to remove clogged pipes is to use small amounts of chemical solutions with high heat of reaction. For example, the reaction of sodium nitrite (2NaNO_2) and ammonium nitrate ($3\text{NO}_2 + 4\text{NH}_3$) or ammonium chloride ($\text{Cl}_2 + 4\text{NH}_3$) is as follows:

A Solution of 3 M High Reactants

Production of SCF400 means nitrogen gas and 879 Btu/m^3 heat per barrel of solution ($879 \frac{\text{MJ}}{\text{m}^3}$)

If this reaction takes place in the presence of hydrate, the heat generated will cause the hydrate to decompose. It should be noted that the reaction produces nitrogen, which can increase the pressure exponentially, and the temperature also rises, which can cause an explosion.

Controlling hydration by reducing pressure: There are generally three ways to control hydration by reducing pressure:

1. In the form of an isotherm in which the pressure drop is extremely slow.
2. As a constant enthalpy that occurs when pressure decreases in a Jules Thompson expansion valve.
3. Iso-topically from which pressure drop occurs in a turbine expander.

The above three processes start for the same pressure drop. Reducing the pressure alone can cause the hydrate to decompose, but in practice the reducing pressure must be supported by the heat entering the system from the environment (air or earth). The actual pressure reduction process is usually between the isotherm and the adiabatic state. Since the decomposed hydrate components have more energy in the vapor-liquid state than the solid phase, according to the first law, the energy required to decompose the hydrate must be provided by the environment (such as a heat exchanger). The main purpose of pressure reduction is to reduce the hydrate pressure to a point where the equilibrium temperature falls below ambient temperature. In this case, the temperature gradient from the environment will cause heat to enter the system and as a result, the hydrate will decompose. Decomposable hydrate can provide the heat required for decomposition from the mass of the hydrate itself, thus reducing the temperature.

From a practical point of view, it is necessary to gradually reduce the pressure of the hydrate from both ends. As an important consequence there should be no large pressure difference during hydration.

Isotherm pressure drop: The isotherm pressure drops results in a high temperature limit for expansion, which is a vertical line. If the ambient temperature rises from its previous state until the hydrate pressure decreases, but the temperature of the decomposing mass of the hydrate cannot increase from its original value, the reduction of the isotherm pressure of the process is extremely slow. Therefore, the environment will provide heat to the system during the decomposition of hydrates. For example, a controlled pressure drops in a long ocean pipeline or S gas pipeline buried to separate hydrates over a period

of days or weeks could be an example of an isotherm pressure drop. As soon as the pressure drops, noticeable ambient heat is supplied to both the hydrate and the steam phase to maintain a constant temperature until the system reaches point A to point B. At point B, the hydrate begins to decompose, and the heat of decomposition of hydrate enters the system to maintain a constant temperature until the decomposition of the hydrate is complete. Further reduction of pressure causes the system to progress to point C (with the need for noticeable heat input to move to the vapor and liquid phase).

Constant enthalpy pressure reduction: Another type of pressure reduction is the constant enthalpy process, which is accompanied by a rapid pressure drop in the absence of a heat exchanger. No heat (Q) or work (WS) is exchanged with the environment for rapid hydrate decomposition in a current system.

Therefore, according to the first law of thermodynamics for a system in steady state ($\Delta H = Q - WS$), the enthalpy changes are zero. According to the constant enthalpy mode, no heat enters the system to cause the temperature to rise and also the system does not do anything to cause the temperature to decrease. The process of constant enthalpy is like an expansion of Jules Thomson. While the Joule-Thomson expansion properties change for different gases, the slope of the fixed enthalpy expansion curve is generally much lower than that of three-phase equilibrium curves (LW-H-V). With this type of pressure drop, most of the gases expand toward the hydrate region. That is, they tend to form hydrates rather than break down hydrates. Inlet heat from the ambient side will be required to increase the temperature (typically at a constant final pressure, for

example at point D) to the two-phase vapor-liquid region [81].

The constant enthalpy mechanism alone will not cause hydrate to decompose

Isentropic pressure reduction: Isentropic pressure reduction ($\Delta S = 0$) is less common than the previous two processes. This process specifies a lower limit for the adiabatic pressure drop ($Q = 0$) as indicated by the line. In this isentropic process, energy is transferred from the system, which is transferred axially.

For example, a reversible turbine expander is used to reduce the temperature under isentropic conditions for a specific pressure drop.

The flow in such a state is usually so fast that it does not allow heat transfer to the environment. Since the entropy change is zero, the conditions of this process are an ideal state and in reality, it is not. In such a case, the process of isentropic expansion causes hydrate formation much faster than constant enthalpy expansion [80].

Therefore, at the end of such a process, heat must be introduced into the system from the environment to decompose the hydrate.

Effect of inhibitors on process of hydrate formation

In a series of experiments, Lederhaus et al. studied the effect of several kinetic inhibitors on the process of hydrate formation of natural gas and showed that hydrate formation is slowed down in the presence of NaCl and polyvinyl caprolactam. Visual observations in these experiments showed that the hydrate obtained in the presence of NaCl contained larger crystals than

the hydrate obtained in the presence of PV Cap. Based on the Lang and Quami model, the reason for hydrate formation at low temperatures and high pressures can be explained. As the temperature decreases, the kinetic energy of the liquid phase molecules decreases and more hydrogen bonds are formed between the water molecules.

Formation of these bonds increases the number of molecular aggregations on the surface. Also, with increasing pressure, the number of gas molecules per unit of water surface increases and the probability of a gas molecule being placed in a suitable cavity due to accidental movement increases and consequently the probability of hydrate formation increases.

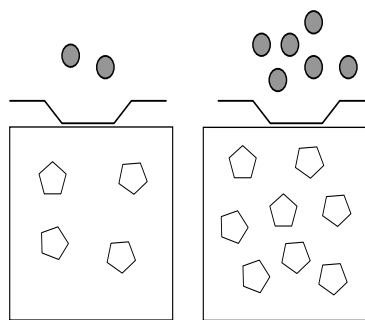
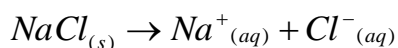


Figure 3. The effect of decreasing temperature on the number of holes in the joint surface of water and gas / The effect of increasing pressure on the probability of gas molecules colliding with the joint surface of water and gas. Based on the experiments of Lederhaus et al. it can be concluded that inhibitors, such as NaCl, can slow down or stop the process of hydrate formation by reducing the number of holes in the surface or, like PV Cap, by blocking these holes. To justify the inhibitory mechanism of NaCl in the process of hydrate formation, the similarity between this phenomenon and water freezing can be used. Pure water begins to freeze at zero degrees Celsius. For this purpose, it is necessary to first create appropriate molecular aggregations of water molecules by

establishing hydrogen bonding. These aggregates will be the units that make up the ice crystal. Salt dissolves rapidly in water and ionizes rapidly, dispersing its positive and negative ions in the liquid phase. These ions generally have high charge densities that can form strong attractions with water polar molecules [82].



As gravity is created between the cations and anions created by the water molecules, each ion is quickly surrounded by six water molecules. Therefore, the presence of cations and anions keeps water molecules out of reach to form molecular arrangements suitable for the ice crystal formation. On the other hand, flooding is a very hot process. The released energy breaks down some of the hydrogen bonds created between the water molecules and destroys the pre-formed molecular aggregations, reducing the rate of the hydrate formation.

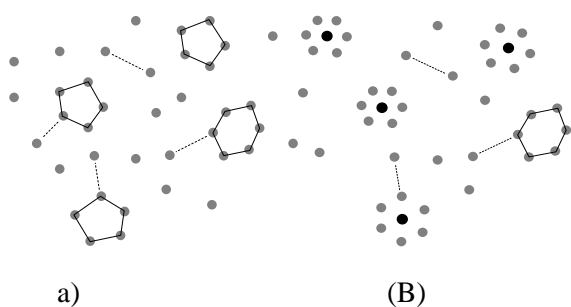


Figure 5. (a) Formation of molecular aggregates in water / (b) flooding of salt ions by dissolution in water

This mechanism can be used to justify the influence of the common salt on the process of hydrate formation. As discussed, formation of the hydrates requires the presence of cavities of water molecules at the water-

gas contact surface. In the presence of NaCl, water molecules are bound by the molecular forces of sodium and chlorine ions. This attraction is stronger than the hydrogen bond between the water molecules, breaking down the molecular accumulations of water. On the other hand, with the release of heat from the water, the temperature of the liquid phase rises locally and removes it from the phase diagram of hydrate formation.

Accordingly, the degree of inhibition of salts depends on the amount of charge on the ions and also the radius of the released ions. Due to the smaller number of hydrogen bonds in accumulations with fewer water molecules, less energy is required to break the bonds and adsorb to the existing positive and negative ions, and therefore small cavities disappear faster. While more bonds in aggregates with more molecules, more energy is required to break. Therefore, we are expected to see larger hydrate crystals at the presence of the NaCl due to the disappearance of small cavities. Therefore, the best inhibitors are those that release the maximum number of cations with the minimum ionic radius.

Table 1. The rate of reduction of solubility of guest molecules by different cations

AP	Ionic radius (Å)	electrical charge	Element
0.67	0.34	+2	Be
0.20	0.57	+3	Al
0.11	0.78	+2	Mg
0.05	1.06	+2	Ca
0.04	0.98	+1	Na
0.02	1.33	+1	K

In addition to the ionic radius and electric charge, the price of salt and its state of being are also important. Among the anions, chlorides, nitrates and sulfates are the most used. An important factor that should be considered in choosing the salt used as an inhibitor is its corrosion. Another disadvantage of salts is that they become thicker due to the heat and precipitate downstream after reaching colder areas.

In other words, these inhibitors are introduced at lower concentrations exactly where hydrate is more likely to form. This polymer is composed of a large monomeric molecule. Due to the presence of oxygen and nitrogen killing electron groups on the benzene ring, the ring electron cloud is attracted to these atoms and some positive charge is applied to the ring hydrogens. Due to the created charge, the molecules of this polymer can establish gravity with the negative charge on the oxygen atoms of the water molecule and block them inside the adsorbed surface cavities [83].

This reduces the number of active points available for nucleation at the surface and reduces the chance of the gas molecule being trapped in these cavities. Due to their large size, these molecules can only be absorbed into larger cavities, leaving small cavities to form hydrates. For this reason, the hydrate formed in the presence of large molecule polymeric inhibitors will consist of finer crystals than the pure solution.

The correlation presented the following experimental equation for how inhibitors affect the hydrate formation process.

$$\Delta T = \frac{K \cdot x}{M(100 - x)}$$

Where ΔT is the rate of reduction of the hydrate formation temperature, k is the specific inhibitor

specificity, M is the inhibitory molecular mass, and x is its inhibitory mass concentration [84-86].

Conclusion

Absence of high sub-cold temperatures in Iran, especially in the Persian Gulf, provides suitable conditions for replacing thermodynamic inhibitors with kinetic inhibitors. Calculations related to the equilibrium line of hydrate formation in gas transmission lines and gas condensate from sea to land in the South Pars Gas Complex are well illustrated by this. Kinetic inhibitors are present in most parts of Iran. Therefore, it is always necessary to consider the limitations of these substances before use; however, the use of these substances can have economic and environmental benefits.

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