United States Patent

[11] 3,547,195

[72] Inventor **Lloyd E. Elkins**
Tulsa, Okla.

[21] Appl. No. **834,900**
[22] Filed **June 19, 1969**
[45] Patented **Dec. 15, 1970**

[73] Assignee **Pan American Petroleum Corporation**
Tulsa, Okla.
a corporation of Delaware

---

[54] **PYROLYTIC PLUGGING OF OIL-BEARING FORMATIONS BY UNDERGROUND COMBUSTION**
8 Claims, No Drawings

[52] **U.S. Cl.** **166/261,** 166/288
[51] **Int. Cl.** **E21b 43/24**
[50] **Field of Search** 166/288, 260, 261, 262, 256, 303, 302

[56] **References Cited**

UNITED STATES PATENTS

2,871,942	2/1959	Garrison et al.	166/260
3,024,840	3/1962	Allen	166/260
3,198,249	8/1965	Willman	166/288X
3,259,188	7/1966	O'Brien	166/288X

Primary Examiner—Stephen J. Novosad
Attorneys—Paul F. Hawley and Beull B. Hamilton

ABSTRACT: In an underground forward combustion process for recovering petroleum from earth formations, more uniform progress of the combustion front through a formation over a wide area is obtained by injecting a water solution of sugar after the combustion operation has been started. The sugar undergoes pyrolysis forming a cohesive solid mass when it becomes heated near the combustion front. The oxidizing gas tends to char this solid, further increasing the plugging of channels and thus providing a more uniform progress of the combustion front. Other organic materials can be used in place of sugar if they undergo pyrolysis to deposit cohesive solids.

PYROLYTIC PLUGGING OF OIL-BEARING FORMATIONS BY UNDERGROUND COMBUSTION

Many methods are used to recover oil from oil-bearing underground formations. In one method, air is injected into the formation and the oil is ignited at the injection well. Continued injection of air causes a combustion front to move through the formation forcing oil ahead of the front to producing wells through which the oil is produced to the surface. The combustion front naturally moves most rapidly through the most permeable zones of the formation. The front reaches the producing wells through the more permeable zones before all the oil is recovered from the less permeable zones. Even in any one zone of uniform permeability, the front tends to streak through in an approximately straight line from an injection well to a producing well without fanning out very far laterally in the zone. In addition, the movement of the combustion front is inherently unstable even in zones of uniform permeability. Once a small section of the front gets ahead of the remainder of the front, this small section tends to move ahead more rapidly than the remainder of the front. This is because the permeability of the formation behind the front is very high compared to the permeability ahead of the front. When a small section of the combustion front gets ahead of the remainder of the front, there is a shorter length of the low permeability portion ahead of this section than ahead of the remaining front. Therefore, flow of fluids is more rapid along the path including this shorter length of low permeability ahead of the advanced section of combustion front and this section moves ahead even more rapidly.

Before a combustion operation is started, movement of the front in zones of different permeability can be made more uniform by injecting a material to form a partial plug in the formation. More of the plugging material goes into the highly permeable zones than into the permeable zones, thus plugging the more permeable zones to a greater degree. The plugging materials for this purpose may be foams, activated silicates, finely divided solids, settable liquid resins, or the like.

Even though a partial plugging operation is used before combustion is initiated, nonuniform progress of the combustion front may develop even in a zone of uniform permeability, as explained above. The problem is to decrease the nonuniform progress of the font after the combustion operation has started. If ordinary plugging techniques are used in the burned-out region around the injection well, the high temperature complicates control of the plugging operations. If a plug is formed near the injection well, the injected gases immediately rearrange themselves into previous patterns as soon as they have penetrated the plugged volume and enter the highly permeable burned-out formation between the plug and the combustion front. If a plug is formed near the combustion zone, control problems due to higher temperatures become extreme.

An object of this invention is to provide a method for forming a partial plug in the burned-out portion of a formation behind an underground forward combustion front. A more specific object is to provide a process for forming a partial plug in the burned-out portion of a formation near an underground forward combustion front. Still other objects will be apparent to the those skilled in the art in view of the following description and claims.

In general, I accomplish the objects of my invention by injecting the injection well and into the formation a water solution of a material, such as a sugar, which undergoes pyrolysis at high temperatures to form a solid cohesive mass in the pores of the formation. Thus, advantage is taken of the high temperature to form the plug near the combustion zone where it is most helpful. This process takes advantage of the high temperature which is a disadvantage in other processes.

Most organic materials undergo pyrolysis at high temperatures. The usual result is a decomposition of the molecules into small fragments which burn in the oxidizing atmosphere of the underground combustion operation. In some organic compounds, such as the sugars, however, the first pyrolysis

reaction is a polymerization. In the case of sucrose, for example, water is eliminated from two hydroxyl groups leading two carbon atoms connected through an ether linkage. Since sugar molecules have several hydroxyl groups, extensive polymerization occurs. Other polyhydroxyl organic compounds are also known to undergo similar polymerization at high temperatures. These include the so-called sugar acids, such as gluconic acid, mannuronic acid, galacturonic acid, and the like. The sugar alcohols, such as sorbitol and mannitol, as well as other polyhydroxy compounds, such as pentaerythritol, and even glycerine, are members of another group of satisfactory products.

Polyamines, such as triaminobenzene, tetraethylene pentamine, and the like, can lose ammonia from two amine groups on heating and form polymers with carbon atoms of different molecules connected through amine linkages. Polyunsaturated acids, such as linoleic and linolenic acids, are known to polymerize upon heating. Water-soluble salts of such acids may also be satisfactory under some conditions. Still other materials which polymerize upon heating will occur to those skilled in the art.

It should be noted that polymerization at high temperature is not the only requirement of the organic compound. It must be soluble to the extent of at least about 1 percent by weight in water. Also, a water solution of the material must be capable of being injected into permeable earth formations. Most natural gums, such as karaya and starch, as well as many synthetic materials, such as sodium carboxymethyl cellulose, form what might be considered water solutions, but these are used in drilling fluids, for example, because they will not enter formations but deposit impermeable cakes on the face of the formation. Such materials are not, of course, satisfactory in my process.

Some organic materials polymerize at temperatures too low for my purpose. For example, the low-temperature reaction product of phenol and formaldehyde polymerizes upon heating to form a cohesive, solid plugging material. Since this reaction takes place at a temperature of only 300° or 400° F., it would deposit in the burned-out formation too far behind the combustion front to be very effective. The organic material should pyrolyze to form a solid at a temperature between about 400° F. and about 800° F. If pyrolysis takes place at a lower temperature, premature plugging can occur too far away from the combustion zone. If pyrolysis does not take place until a temperature of about 800° F. is reached, the plug can form so close to the combustion front that there is danger it will be quickly burned out in the highly oxidizing atmosphere.

Summarizing these conditions, the plugging agent must be a water-soluble organic material capable of entering permeable formations in water solution and undergoing pyrolysis at a temperature between about 400° F. and about 800° F. to form a cohesive solid mass in the pores of the formation.

The suitability of a material can be easily determined by passing a dilute aqueous solution (2 to 10 percent by weight) of the material through a sand-packed tube while heating the tube to a temperature of 400° to 800° F. If the tube becomes plugged, the material is, of course, satisfactory for my purposes.

While any of the above-mentioned classes of materials can be used in my process under at least some conditions, the two materials which are greatly preferred for my purposes are sucrose and glucose, preferably in the form of raw sucrose and corn syrup, respectively. These sugars are very inexpensive, particularly in the raw form, but are sufficiently pure to permit their solutions to be injected easily into formations. Some natural sugar solutions, such as molasses, are very attractive from the standpoint of cost, but most of them must be carefully filtered before use to avoid plugging the formation face of the injection well.

A tube was filled with tar sand from the Athabasca field in Alberta, Can. The tar had been previously burned from this sand. A 12-inch length of the tube was surrounded with a

heater. Thermocouples were attached to this section of the tube so the temperature could be measured. A solution of molasses in water was injected into the packed tube together with air. The molasses solution contained about 10 percent sugars by weight. This solution was carefully filtered before use to avoid plugging the tube with solids suspended in the molasses. Flow rates were about 3 milliliters per hour for the molasses and about 29 milliliters per hour for the air. The air volume was measured at means pressure in the tube. A back pressure of about 800 pounds per square inch gauge was held on the tube. The temperature was increased in steps and the pressure differential across the tube at constant flow volumes was measured. At temperatures up to 400° F., the pressure drop remained at about 6 p.s.i.g. When the temperature was raised to 600° F., the pressure drop increased slowly to 85 p.s.i.g. in 72 hours. Raising the temperature to 700° F. resulted in a sharp increase of pressure drop to about 400 p.s.i.g. in about 8 hours.

When the flow test was repeated with a 200 p.s.i.g. back pressure, the rapid pressure drop occurred at about 530° F. Study of all the information indicated that rapid plugging occurred at approximately the temperature at which the water flashed into steam. Apparently, little pyrolytic dehydrolysis of sugars can take place while the sugars are dissolved in liquid water. As soon as the water flashes into the vapor phase, however, pyrolytic loss of water from the sugar occurs with consequent polymerization and formation of a cohesive solid mass which plugs the formation pores.

A repeat of the second test using nitrogen in place of air resulted in plugging at about the same temperature but somewhat more slowly. This shows that the charring action of the oxygen in the air is helpful in the plugging operation.

A repeat of the second test, using only enough molasses to provide 4 percent sugars in the solution, produced the same results as in the second test, except that the lower sugar concentration formed the plug more slowly. This test was terminated and the tube was cooled before complete plugging could take place. Flow of air at various temperatures was then measured to determine the stability of the plug. Results are shown in Table I.

TABLE I

Temperature, ° F.:	Effective permeability to air, md.
76	.06
300	.22
400	300.00
600–625	1,250.00
700	1,440.00
800	4,050.00

The final permeability at 800° F. was only slightly less than the original permeability before plugging. It will be obvious, therefore, that if the plug does not form at a temperature below about 800° F., there is some danger that the plug will be burned out before it can do much good. It should be noted, however, that about 5,000 pore volumes of air passed through the plugged zone in this test, so it is unlikely that a well-formed plug would burn out prematurely at 800° F. in actual operations. As previously explained, however, materials which pyrolyze below about 800° F. should be used to avoid this danger.

In another test, no gas was injected with the molasses solution. In this test, a very dilute solution of molasses was used which provided only about 2 percent by weight of sugars. In this test, a plug formed at 450° F. The plug remained permanent when exposed to compressed air pressure for 70 hours at 450° F. When the temperature was increased to 600° F., however, the compressed air broke through the plug. Obviously, this plug was not as stable as those in previous tests. This may have been due either to the very low concentration of sugar, to the lack of air, or to the formation of the plug at very low temperature. Since in an actual application of the plugging technique, the temperature will not increase after the plug formed, the use of a batch of molasses solution followed by air is obviously a satisfactory way of forming an effective plug in the formation behind the combustion front.

In still another test using no gas with the injected molasses solution, a plug was formed very slowly at 600° F. using a molasses solution so dilute that it contained only a little over 1 percent sugars. This plug was also somewhat unstable when subjected to compressed air at 600° F. It is obvious from this test that the sugar concentration in the plugging solution should be at least about 1 percent by weight and preferably considerably higher.

Concentrated solutions of organic materials, such as sugars, are very viscous. If sugar solutions are to be injected at a high rate into and through earth formations, the sugar concentration should be not more than about 20 percent be weight. A concentration as low as 1 percent has been shown to give at least some plugging. Preferably, the sugar concentration should be about 2 to 10 percent by weight. The sugar may be a single sugar or a mixture of sugars. Mixtures of other pyrolytic plugging materials with each other or with sugars can also be used.

When a treatment is being designed, the volume of sugar solution will depend upon the concentration of sugar in the solution and the volume of pore space to be plugged. Since the object is to plug streaks, a much smaller volume of solution can be used than in some processes where the entire formation is to be plugged. If, for example, a streak **12** feet high and **20** feet wide is to be plugged for a distance of 1 foot, and if the porosity is 36 percent, the volume of pore space is about 86.5 cubic feet. This volume of sucrose with a density of 1.58 grams per milliliter weighs about 8500 pounds. If this amount of sugar is injected as a ten percent by weight solution, the solution weight is about 85,000 pounds and the volume is about 10,000 gallons, or approximately 240 barrels (42 U.S. gallons per barrel). If a 2 percent solution is to be used, the volume should be five times as great. If a 20 percent solution is to be used, the volume should be one-half as great. If an injection well is surrounded by four producing wells and four streaks are expected, the volume should be about four times as great. The volume should also be adjusted for the porosity of the formation to be treated for the estimated width and height of the streak and for the length of the desired plug.

As the sugar begins to undergo pyrolysis and deposite in the pores of the main flow channels, flow through these pores is restricted and is increasingly diverted to other flow paths. Therefore, a complete plug is not necessary. A partial plug provides considerable benefits. If a complete plug of any length forms, even a fraction of an inch, flow is completely diverted from the plugged flow channel and the plug length does not increase. It will be apparent that a complete plug a foot long would be difficult to form in my process. For these reasons, the volumes of sugar solution suggested above are larger than necessary to produce at least some benefits.

Also, as the sugar undergoes pyrolysis, it foams. Of course, a smaller volume of solid in the form of foam is required to fill a given pore volume than if the solid is in a dense unfoamed state. Again, this means that the volumes of solution suggested above are somewhat larger than are actually required.

The solution may be injected as a single batch, or it may be injected continuously with the injected air. The treatment may be repeated to plug new channels as they form during the combustion operation.

A considerable volume of water should follow the sugar solution into the formation. If the solution is simply injected into the formation and is then followed by air only, the solution will remain near the well bore to establish the irreducible minimum water saturation of from about 10 to about 30 percent in the pores of the formation. Of course, this is satisfactory when the combustion zone is near the injection well, but when the combustion zone is not near the injection well, water

should be injected after the sugar solution to displace the solution ahead toward the combustion zone. The displacing water may be alternated with air.

In one very advantageous way of conducting an underground combustion operation, air and water are alternately injected into the formation. In such a process, a batch of sugar solution can be occasionally substituted for one of the batches of water to obtain the plugging action of the sugar near the combustion zone.

It is possible to use the process to form a plug by injecting the solution into the formation from the producing well. A heated zone precedes a forward combustion front for some distance in the formation. When the sugar solution reaches a hot enough portion of this heated zone, a plug will be formed. It should be noted, however, that the plug will be formed near the combustion zone which will quickly move through the plugged zone. At this time, the plug will be burned out. Therefore, it is usually best to use other plugging techniques to reduce the permeability of high-flow capacity channels at the producing well. It will be apparent that my process can be used in combination with other plugging processes applied to either a producing well or an injection well. For example, foams can be used to provide a more uniform injectivity of air into zones of different permeability, these foams being used before the combustion operation begins. My process can then be used to plug channels which form after the combustion operation has started.

My process obviously is applicable only to forward combustion operations where the combustion zone moves in the direction of flow of injected fluids. It is not applicable to reverse combustion operation where the sugar solution would not pass through a portion of the formation hot enough to form a plug before the solution reached the combustion zone where the sugar would burn.

My process will be better understood from the following example. An injection well is surrounded by four producing wells. All the wells penetrate an oil-bearing formation about 100 feet thick. Combustion has been initiated in the oil-bearing formation at the bottom of the injection well and air has been injected into this well for about 60 days, together with occasional batches of water. In order to reduce channeling of this air through the formation, a water solution of molasses is injected into the formation through the injection well. The solution contains about 75 percent water and about 25 percent molasses, both percentages being by volume. The molasses contains about 40 percent by weight of sugars, so the final water solution contains about 10 percent by weight of sugars. The water solution is carefully filtered before use to avoid plugging the face of the oil-bearing formation at the injection well. The volume of solution is about 20,000 gallons. As soon as the solution is introduced into the injection well, injection of air with occasional batches of water is resumed. The molasses treatment is repeated every 60 days until breakthrough of combustion zone occurs into the producing wells. This takes place about 14 months after initiating the combustion. The time of breakthrough and the oil production recovered to breakthrough are greatly increased over the values which are usual without the plugging action.

Several alternates and variations have been described. These are presented by way of example only. Still other alternates and variations will occur to those skilled in the art. Therefore, I do not wish to be limited to the examples given but only by the following claims.

I claim:

1. In a forward combustion process in which an oxygen-containing gas is injected through an injection well and into an oil-bearing formation to support a combustion zone which moves through the formation displacing oil ahead of the combustion zone to a producing well from which oil is produced to the surface, the improvement comprising injecting through said injection well and into said formation after the combustion satisfactory proceeded for some time, and while combustion is continuing, an aqueous solution of an organic material capable of entering the pores of the formation, said material being pyrolyzable at a temperature between about 400°F. and about 800°F. to form a cohesive solid mass, whereby as said solution approaches the combustion zone, the organic material pyrolyzes to plug the principal flow channels, thus diverting flow into other portions of the formation and decreasing channeling tendencies.

2. The method of claim 1 in which said organic material is filtered molasses.

3. The method of claim 1 in which said organic material is a polyhydroxy compound.

4. The method of claim 3 in which said polyhydroxy compound is a sugar.

5. The method of claim 4 in which said sugar is sucrose.

6. The method of claim 4 in which the concentration of said sugar is between about 1 and about 20 percent by weight in said aqueous solution.

7. The method of claim 1 in which said solution of an organic material is followed into said formation by water injected to displace said solution ahead toward said combustion zone.

8. The method of claim 7 in which said water is injected as small batches alternated with oxygen-containing gas.