

Abstract

A hydroformylation process having improved stability involving reacting one or more reactants, such as an olefin, with carbon monoxide and hydrogen in the presence of a hydroformylation catalyst, to produce a reaction product fluid comprising one or more products, preferably aldehydes; wherein said process is conducted in a region of the hydroformylation rate curve that is negative or inverse order in carbon monoxide; and wherein total pressure is controlled at a predetermined target value and/or vent flow rate is controlled at a predetermined target value, by adjusting a flow of a carbon-monoxide containing inlet gas, so as to prevent sudden changes and/or lessen cycling of process parameters, for example, reaction rate, total pressure, vent flow rate, temperature, or a combination thereof.

CLAIMS:

1. A hydroformylation process comprising reacting one or more reactants, carbon monoxide, and hydrogen in the presence of a hydroformylation catalyst to produce a reaction product fluid comprising one or more products, wherein said process is conducted at a carbon monoxide partial pressure such that reaction rate increases as carbon monoxide partial pressure decreases and the reaction rate decreases as carbon monoxide partial pressure increases; and wherein the following process steps are conducted to stabilize reaction rate, total pressure, vent flow rate, reaction temperature, or a combination thereof; the process steps comprising at least one of the following process control schemes selected from:

Scheme A:

- (a1) establishing a target total pressure;
- (a2) detecting the total pressure and determining the difference between the detected total pressure and the target total pressure; and
- (a3) based on the pressure difference measured in step (a2), manipulating a feed flow of gas comprising carbon monoxide to adjust the detected total pressure essentially to the target total pressure; and

Scheme B:

- (b1) establishing a target vent flow rate;
- (b2) detecting the vent flow rate and determining the difference between the detected vent flow rate and the target vent flow rate; and
- (b3) based on the vent flow rate difference measured in step (b2), manipulating a feed flow rate of gas comprising carbon monoxide to adjust the detected vent flow rate essentially to the target vent flow rate.

2. The process of Claim 1 wherein process steps (a1) through (a3) and process steps (b1) through (b3) are all implemented so as to adjust the detected total pressure to the target total pressure and to adjust the detected vent flow rate to the target vent flow rate.

3. The process of Claim 1 wherein one or more olefinic unsaturated compounds are contacted with carbon monoxide and hydrogen to prepare one or more aldehydes.

4. The process of Claim 3 wherein the olefinic unsaturated compound comprises from 3 to 20 carbon atoms.

5. The process of Claim 1 wherein the hydroformylation catalyst comprises a metal-organophosphorus ligand complex catalyst.

6. The process of Claim 5 wherein the hydroformylation catalyst comprises a metal-organopolyphosphite ligand complex catalyst.

7. The process of Claim 6 wherein the hydroformylation catalyst comprises a rhodium-organopolyphosphite ligand complex catalyst.

8. The process of Claim 1 wherein the target total pressure is selected from a range of pressures in a region of steepest positive slope of a graph of Total Pressure versus Synthesis Gas Feed Flow Rate.

9. The process of Claim 1 wherein a minimum target vent flow rate is selected as the vent flow rate equal to the input stoichiometric excess of hydrogen and inerts.

10. The process of Claim 1 wherein a primary source of carbon monoxide is provided to the process to satisfy essentially the stoichiometric requirements of the hydroformylation process, and the detected total pressure is adjusted to the target total pressure by means of a secondary source of a carbon monoxide-containing gas.

11. The process of Claim 10 wherein the primary source of carbon monoxide comprises a primary feed of syngas to the reactor; and optionally, wherein the secondary source of carbon monoxide-containing gas comprises a syngas feed or a pure carbon monoxide feed, or a feed comprising carbon monoxide and an inert gas.

12. The process of Claim 1 wherein the total pressure is controlled by adjusting the flow rate of a carbon monoxide-containing inlet gas, while the vent flow rate of discharged gas from the reactor is maintained at a constant flow rate.

13. The process of Claim 1 wherein the vent flow rate of a discharged gas from the reactor is controlled by adjusting the flow rate of a carbon monoxide-containing gas fed to the reactor, while maintaining the target total pressure.

14. The process of Claim 1 wherein the hydroformylation process is conducted in a plurality of continuous stirred tank reactors connected in series, wherein the total pressure is detected by a detection means located on one or more of the reactors in series, and a signal is transmitted to a carbon monoxide inlet line to one or more of the reactors in series, so as to adjust the total pressure over the plurality of reactors to the target pressure.

15. The process of Claim 1 wherein the hydroformylation process is conducted in a plurality of continuous stirred tank reactors connected in series, wherein the vent flow rate is

detected by a detection means located in a vent line from one or more of the reactors in series, and a signal is transmitted to a carbon monoxide inlet line to one or more of the reactors in series, so as to adjust the vent flow rate over the plurality of reactors to the target vent flow rate.

16. The process of Claim 1 wherein the hydroformylation process is conducted in a plurality of continuous stirred tank reactors connected in series, wherein the total pressure is detected by a detection means located on one or more of the reactors in series, and a signal is transmitted to a carbon monoxide inlet line to one or more of the reactors in series, so as to adjust the total pressure over the plurality of reactors to the target pressure; and wherein the vent flow rate is detected by a detection means located in a vent line from one or more of the reactors in series, and a signal is transmitted to a carbon monoxide inlet line to one or more of the reactors in series, so as to adjust the vent flow rate over the plurality of reactors to the target vent flow rate.

17. The process of Claim 1 wherein the carbon monoxide partial pressure is selected in the inverse order region of the hydroformylation rate curve corresponding to a hydroformylation reaction rate at the maximum or within 50 percent of the maximum rate, as determined from a plot of hydroformylation reaction rate versus carbon monoxide partial pressure.

18. A hydroformylation process comprising reacting in a reaction zone one or more olefinic unsaturated compounds with carbon monoxide and hydrogen in the presence of a metal-organopolyphosphite ligand complex catalyst and optionally a free organopolyphosphite ligand to produce a reaction product fluid comprising one or more aldehydes, and separating in at least one separation zone the one or more aldehydes from the metal-organopolyphosphite ligand complex catalyst and the optional free organopolyphosphite ligand, the improvement comprising: conducting the hydroformylation process at a carbon monoxide partial pressure such that reaction rate increases as carbon monoxide partial pressure decreases and reaction rate decreases as carbon monoxide partial pressure increases; and wherein the following process steps are conducted to float the carbon monoxide partial pressure so as to stabilize reaction rate, total pressure, vent flow rate, reaction temperature, or a combination thereof; the process steps comprising at least one of the following process control schemes selected from:

Scheme A:

- (a1) establishing a target total pressure;
- (a2) detecting the total pressure, and determining the difference between the detected total pressure and the target total pressure; and
- (a3) based on the pressure difference measured in step (a2), manipulating a feed flow of gas comprising carbon monoxide to adjust the detected total pressure essentially to the target total pressure;

Scheme B:

- (b1) establishing a target vent flow rate;
- (b2) detecting the vent flow rate, and determining the difference between the detected vent flow rate and the target flow rate; and
- (b3) based on the vent flow rate difference measured in step (b2), manipulating a feed flow of gas comprising carbon monoxide to adjust the detected vent flow rate essentially to the target vent flow rate.

19. The process of Claim 18 wherein process steps (a1) through (a3) and process steps (b1) through (b3) are all implemented so as to adjust the detected total pressure essentially to the target total pressure and to adjust the detected vent flow rate essentially to the target vent flow rate.

20. The process of Claim 18 wherein the olefin comprises from 3 to about 20 carbon atoms.

21. The process of Claim 18 wherein the metal of the metal-organopolyphosphite complex catalyst is rhodium.

22. The process of Claim 18 wherein the carbon monoxide partial pressure ranges from about 1 psia (6.8 kPa) to about 1,000 psia (6,800 kPa).

23. An apparatus for stabilizing a hydroformylation process comprising:
a reactor comprising a means for feeding one or more reactants; a means for feeding a synthesis gas; optionally, a means for feeding a secondary source of carbon monoxide; a means for feeding a catalyst solution; a means for venting reaction and inert gases; a means for withdrawing a reaction fluid; a means for measuring total gas pressure; and a means for measuring vent flow rate of reaction and inert gases; the apparatus further comprising at least one of the following design schemes selected from:

Design A:

- (a1) a means for determining a pressure differential between a target total gas pressure and the measured total gas pressure;
- (a2) a means for generating a signal corresponding to the pressure differential;
- (a3) a means for receiving the signal from (a2) and for determining and sending an output signal to manipulate the flow rate of synthesis gas and/or secondary source of carbon monoxide to adjust the measured total pressure to the target total pressure;

Design B:

- (b1) a means for determining a vent flow rate differential between a target vent flow rate and the measured vent flow rate;
- (b2) a means for generating a signal corresponding to the vent flow rate differential;
- (b3) a means for receiving the signal from (b2) and for determining and sending an output signal to manipulate the flow rate of synthesis gas and/or secondary source of carbon monoxide to adjust the measured vent flow rate to the target vent flow rate.

24. The apparatus of Claim 23 comprising all of design features (a1) through (a3) and design features (b1) through (b3).

25. The process of Claim 1 wherein the process is conducted at a temperature greater than 50°C and less than 120°C.

26. The process of Claim 1 wherein the hydroformylation catalyst comprises rhodium metal and an organopolymphosphite ligand, such that the rhodium metal is employed in a concentration from 10 to 500 parts per million metal, calculated as free metal in the hydroformylation reaction fluid.

27. The process of Claim 1 wherein the hydroformylation catalyst comprises a metal and an organopolymphosphite ligand, such that the ligand is employed in from 1.1 to 4 moles ligand per mole of metal present in the reaction fluid, such amount of ligand being the sum of both free ligand and ligand complexed to the metal in the reaction fluid.

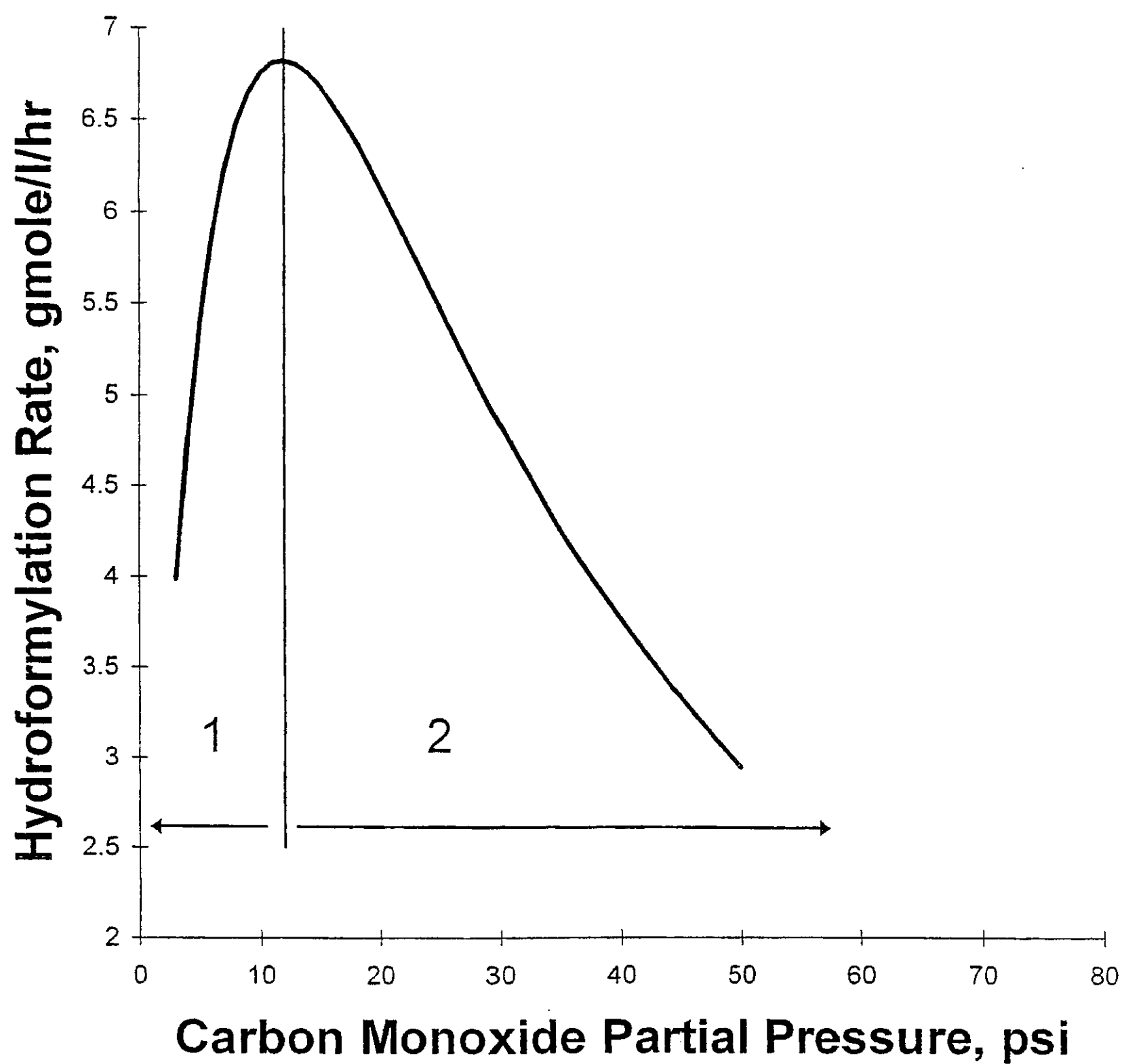
28. The process of Claim 1 wherein the partial pressure of carbon monoxide ranges from 15 psia (103.4 kPa) to 100 psia (689 kPa).

Dated this 2 day of February 2007


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FIG 1

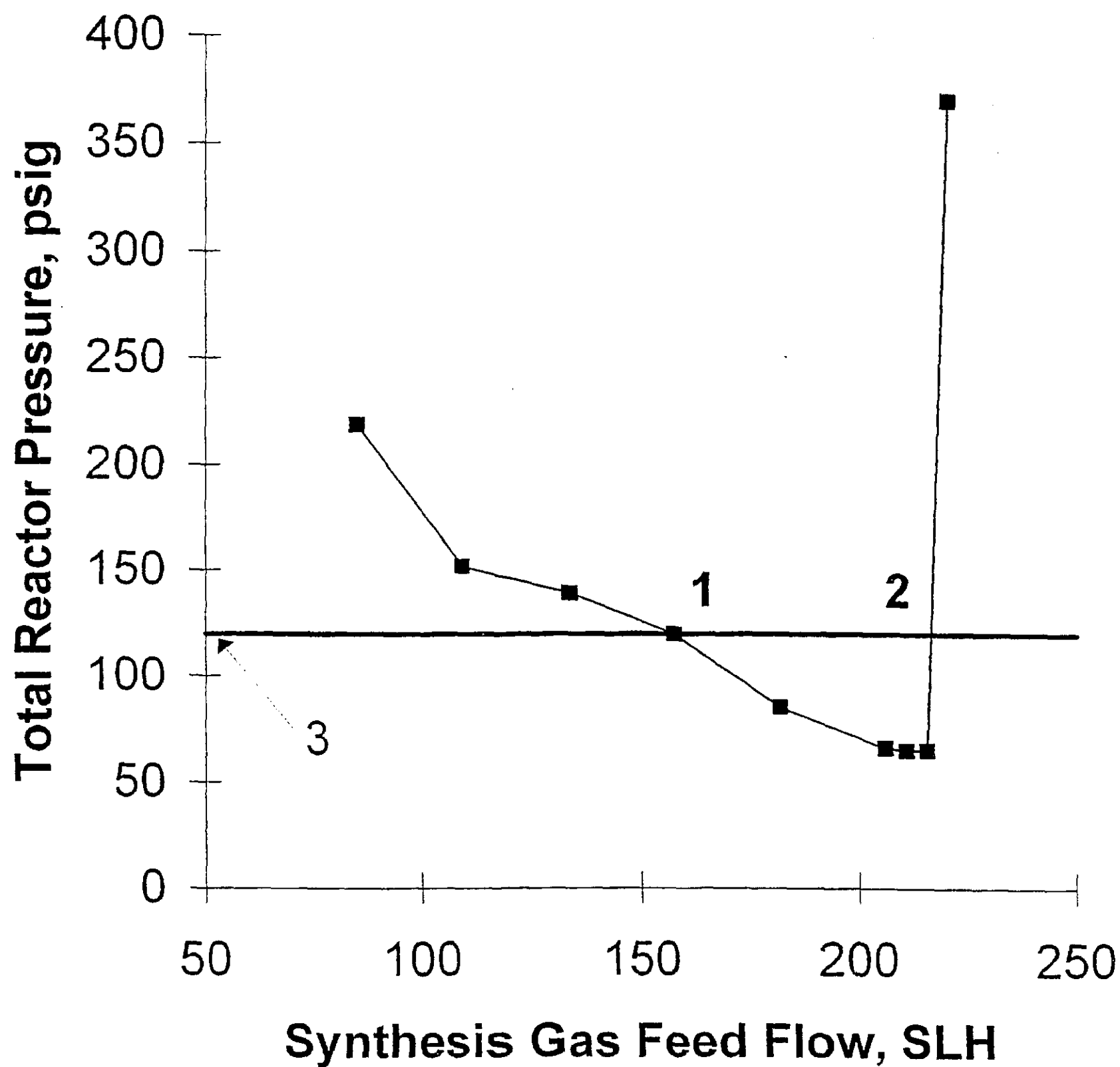


1. Positive order region
2. Negative or inverse order region


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FIG 2

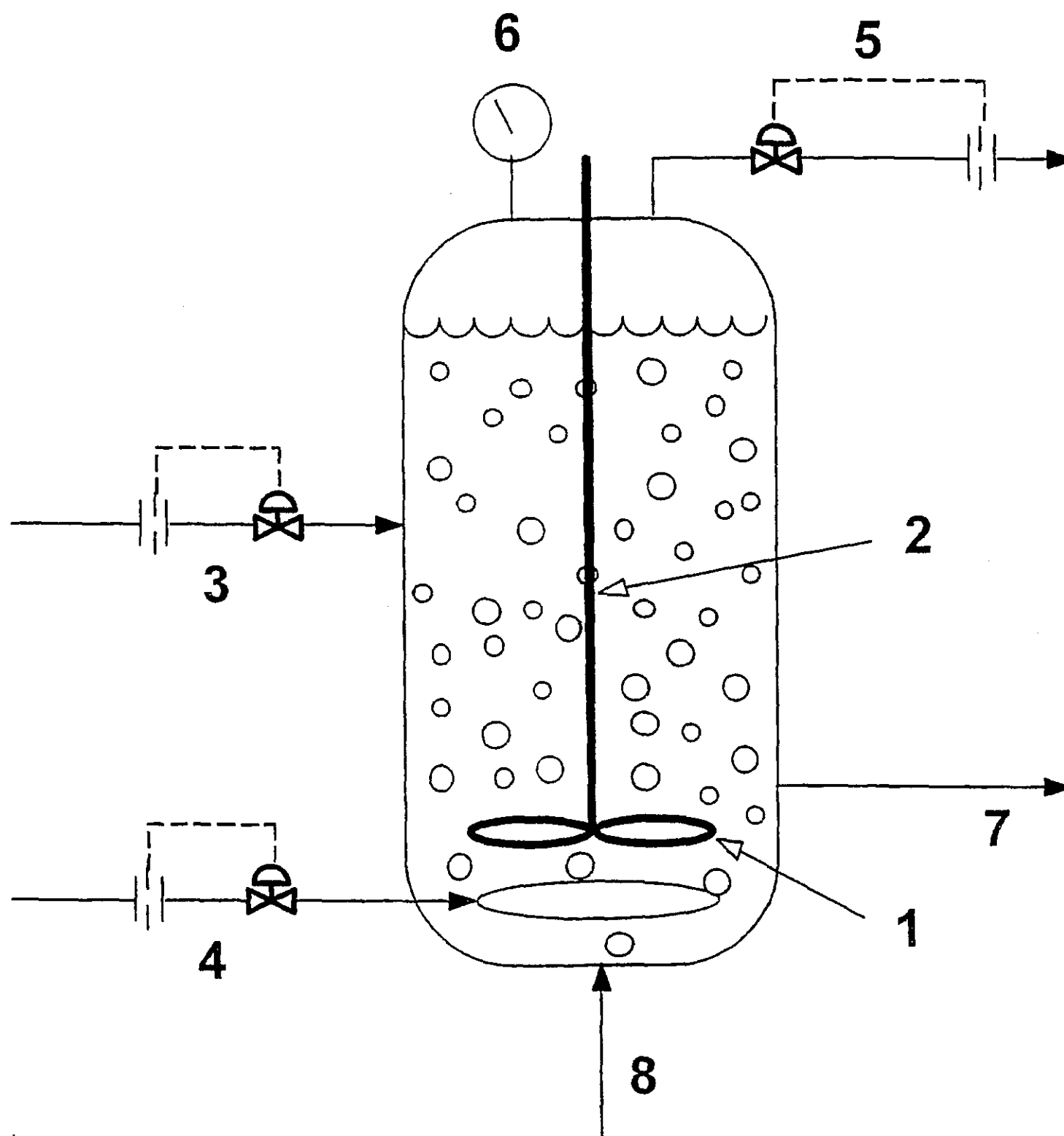


1. Minimum base synthesis gas feed flow rate
2. Maximum base synthesis gas feed flow rate
3. Target total reactor pressure

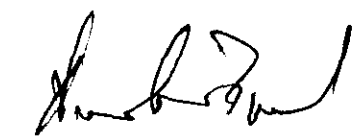

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FIG 3

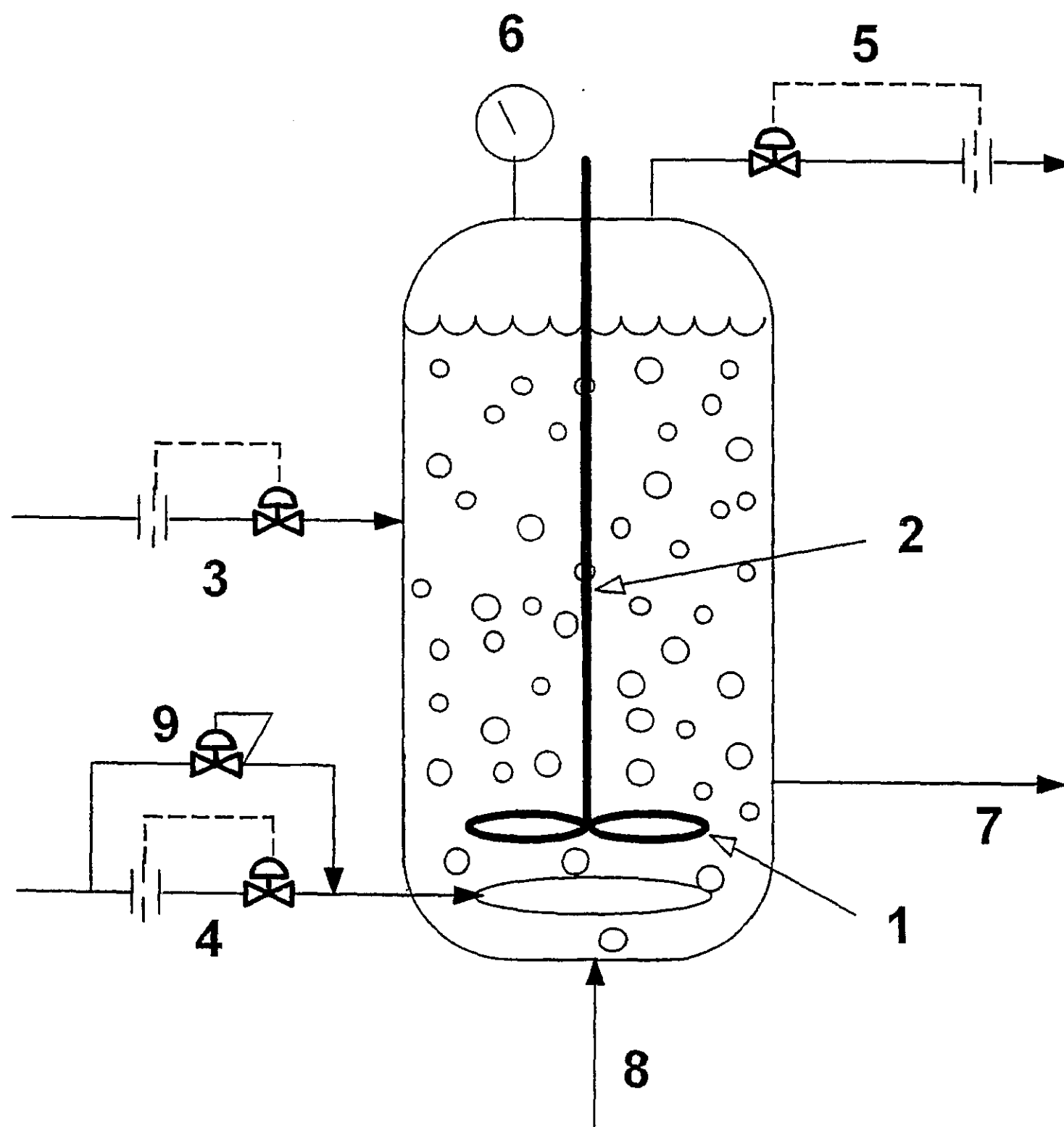


1. Impeller
2. Impeller shaft
3. Propylene feed line and feed flow control
4. Syngas feed line, sparger and feed flow controller
5. Vent flow line and vent flow control
6. Total pressure sensor
7. Exit line for product solution/catalyst to product recovery system
8. Feed line for catalyst returned from product recovery system



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FIG 4

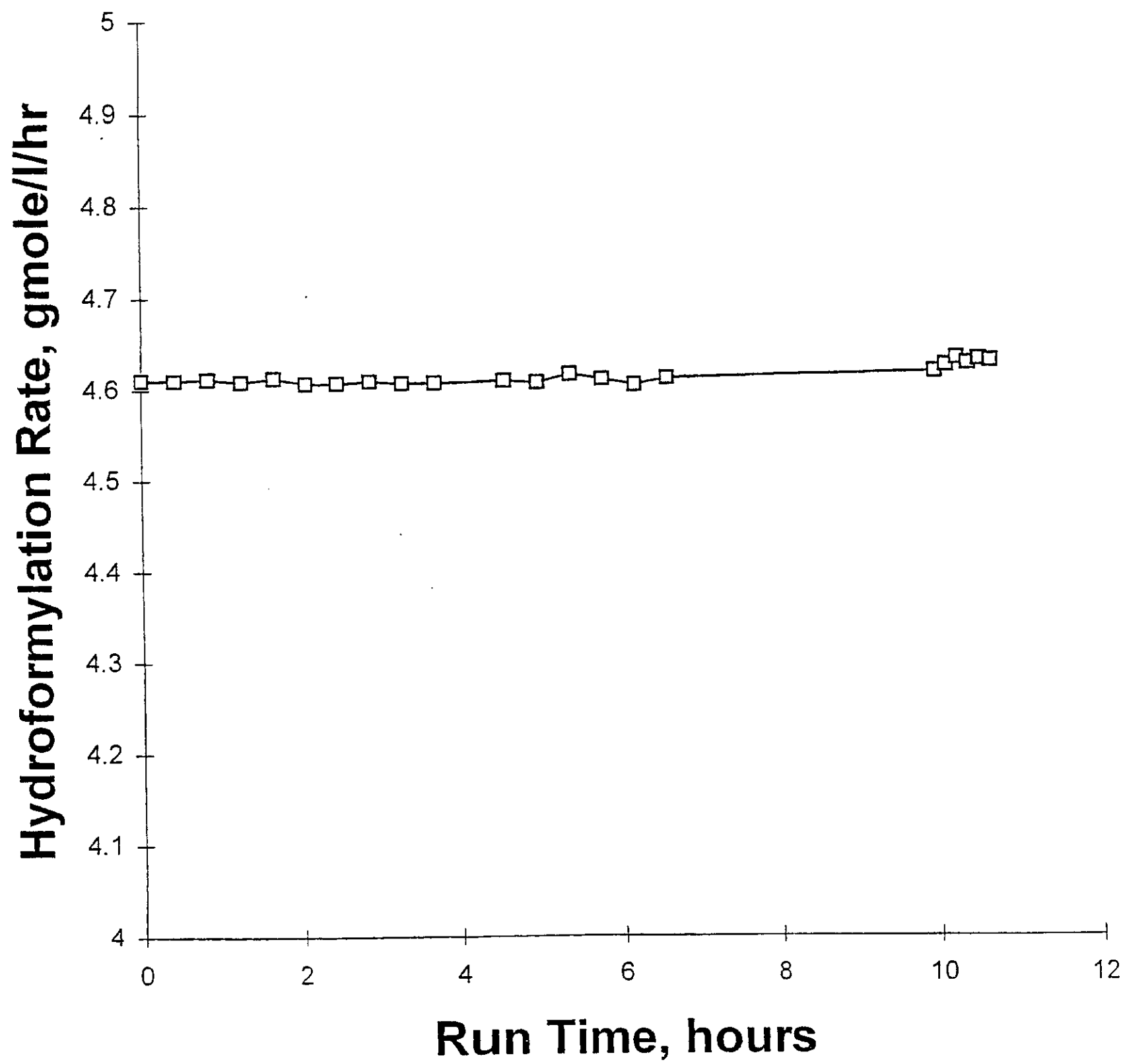



1. Impeller
2. Impeller shaft
3. Propylene feed line and feed flow control
4. Syngas feed line, sparger and feed flow controller
5. Vent flow line and vent flow control
6. Total pressure sensor
7. Exit line for product solution/catalyst to product recovery system
8. Feed line for catalyst returned from product recovery system
9. Reactor total pressure control


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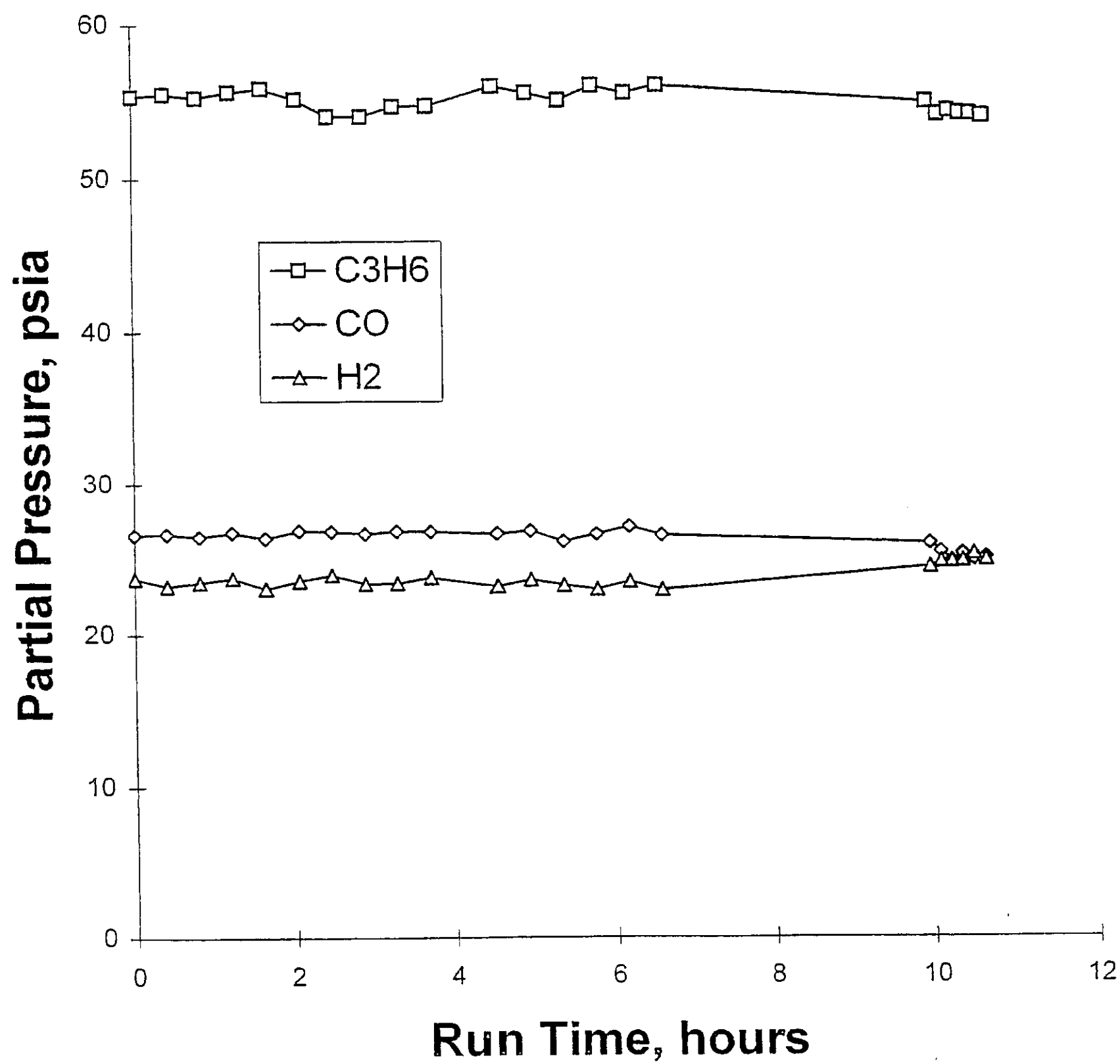
FIG 5





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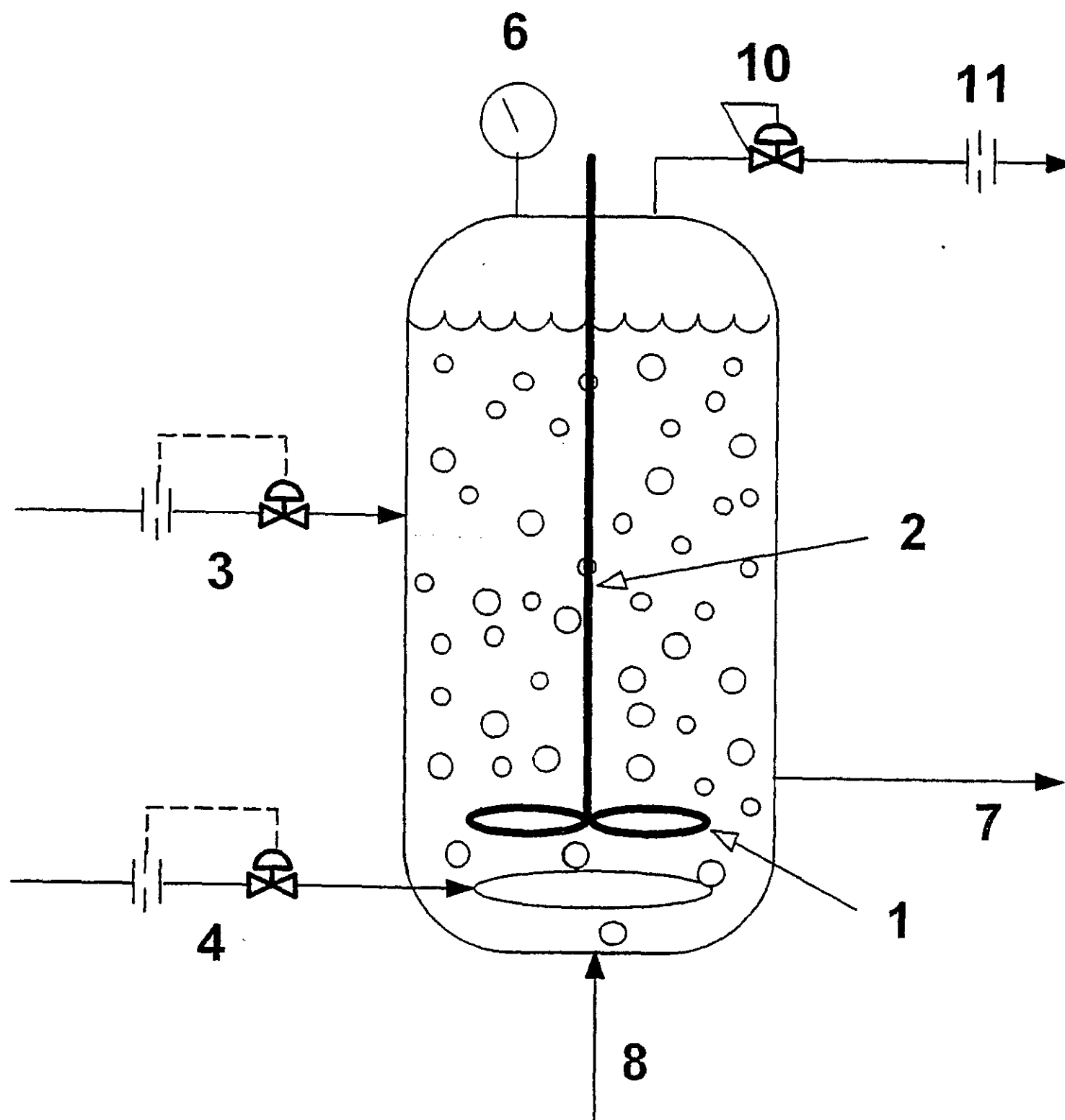
FIG 6




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FIG 7

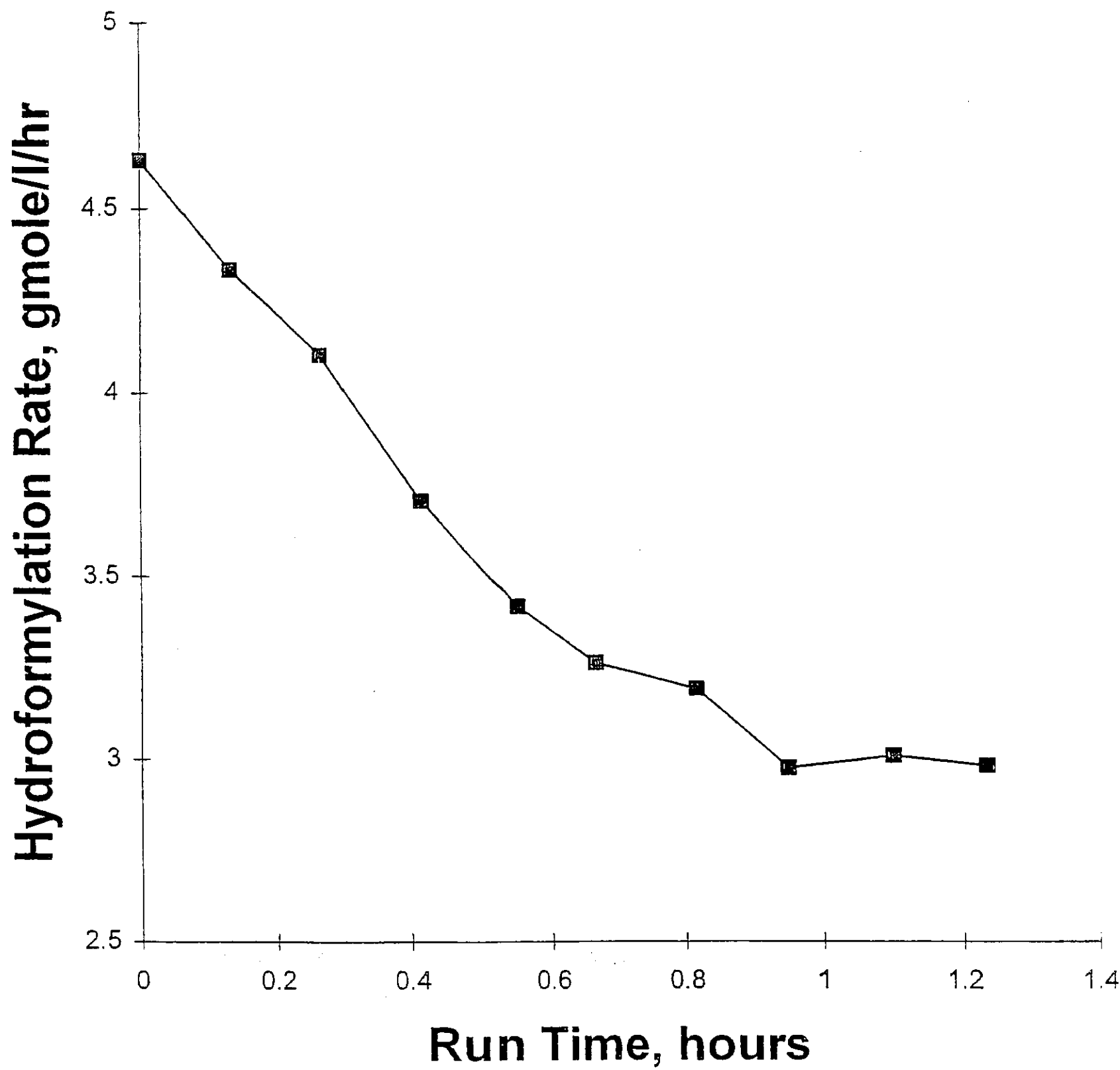



1. Impeller
2. Impeller shaft
3. Propylene feed line and feed flow control
4. Syngas feed line, sparger and feed flow controller
6. Total pressure sensor
7. Exit line for product solution/catalyst to product recovery system
8. Feed line for catalyst returned from product recovery system
10. Reactor total pressure control
11. Reactor vent flow sensor

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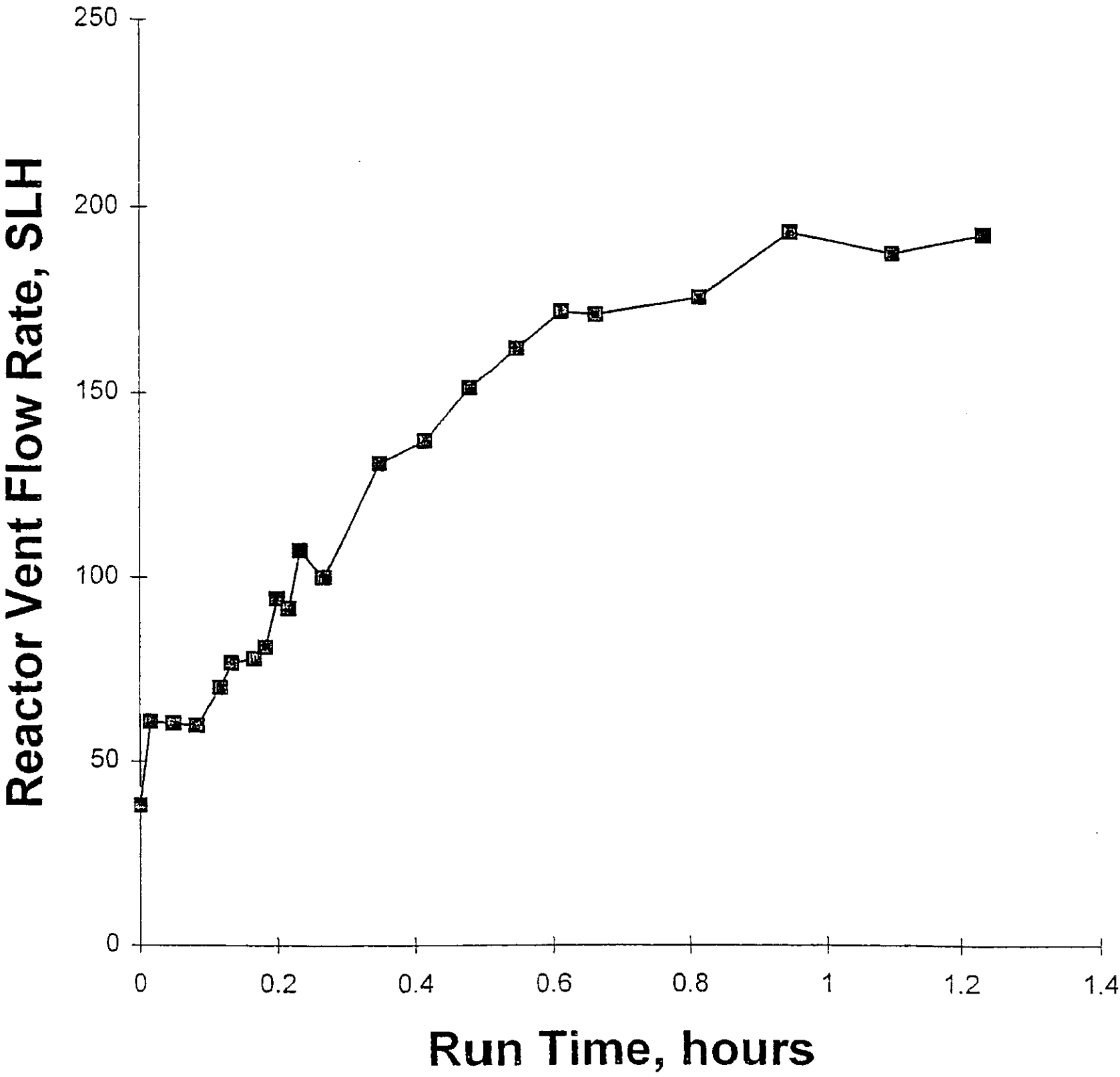
FIG 8




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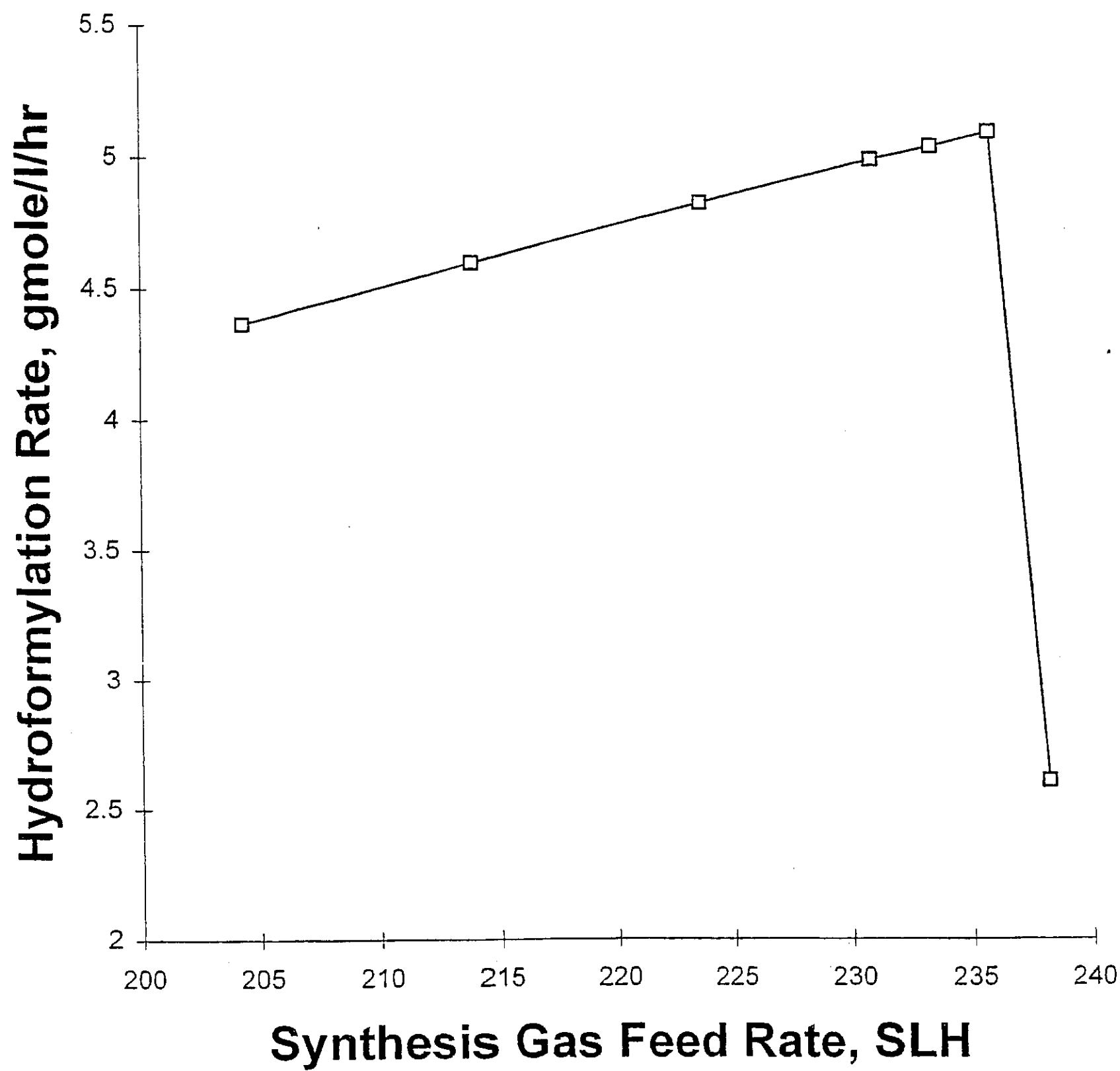
FIG 9




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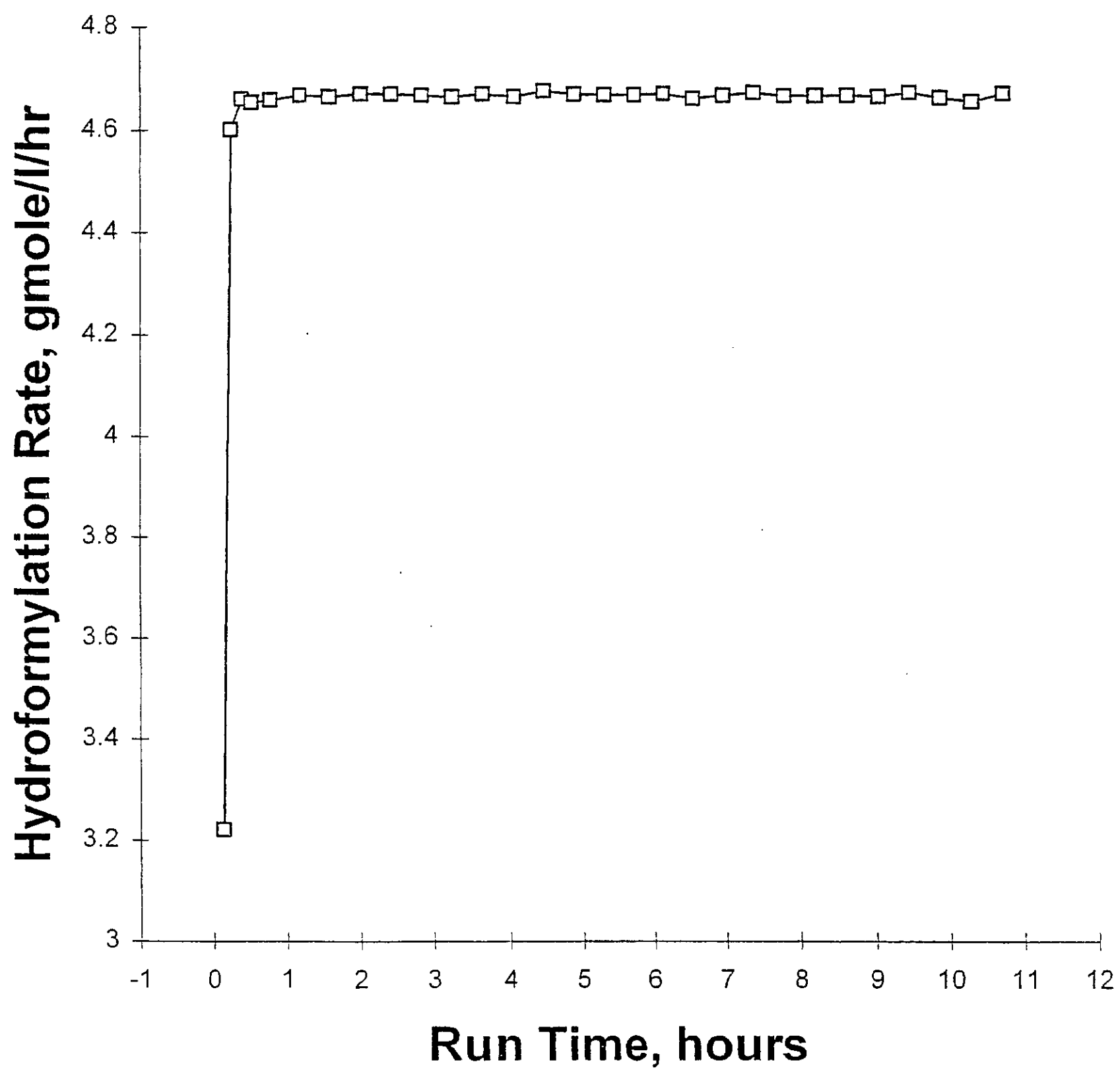
FIG 10



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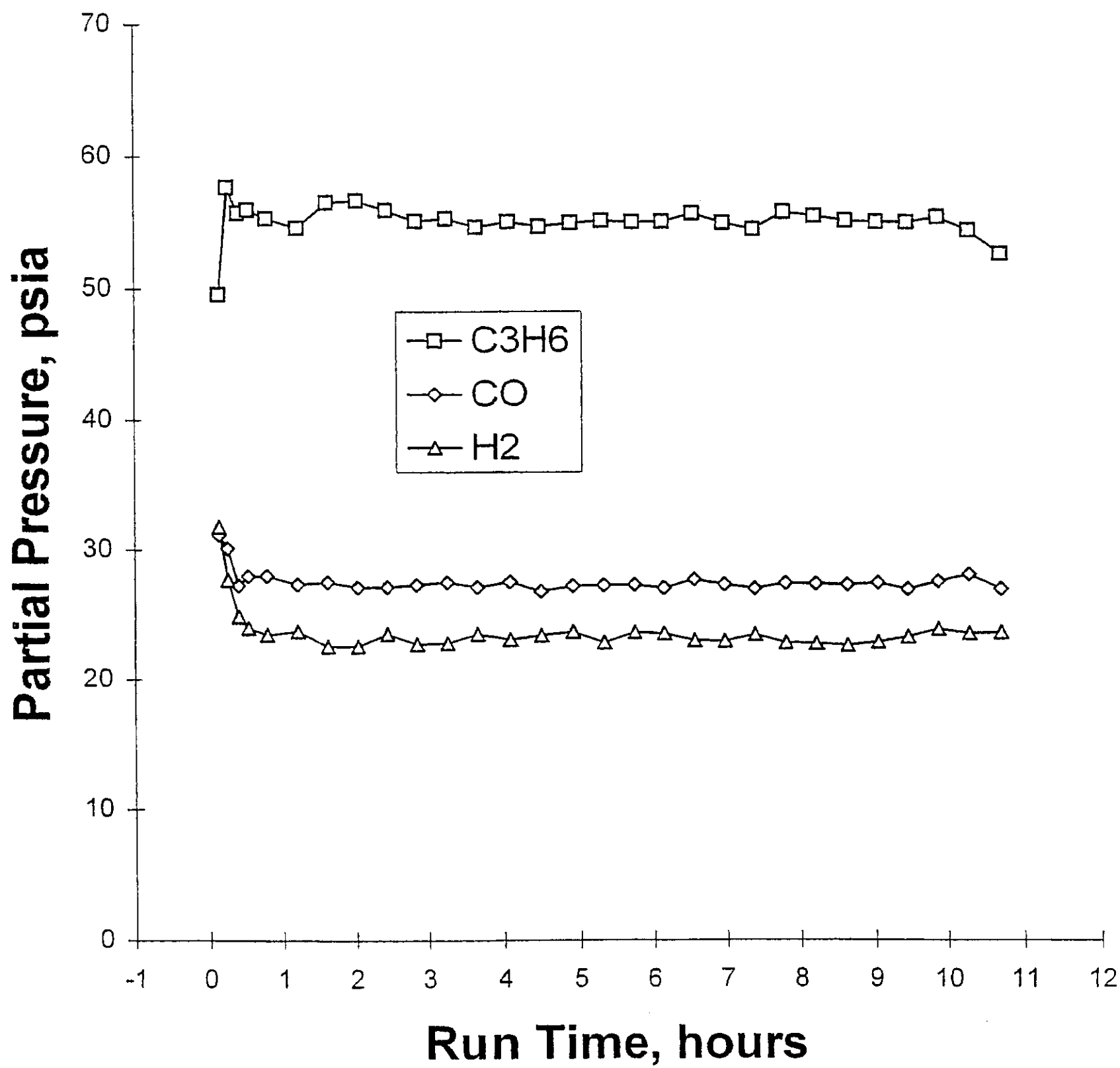
FIG 11




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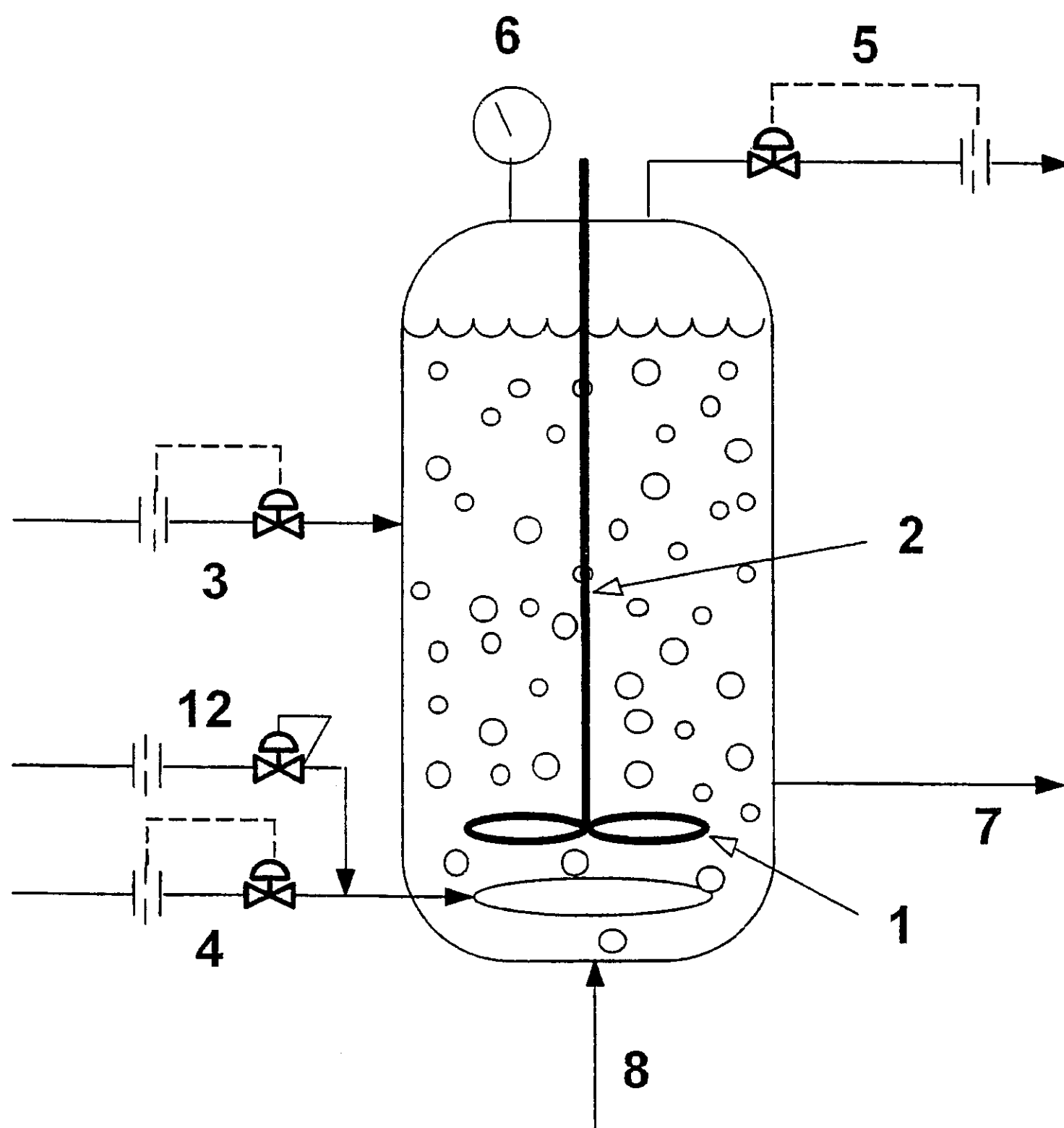
FIG 12





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FIG 13

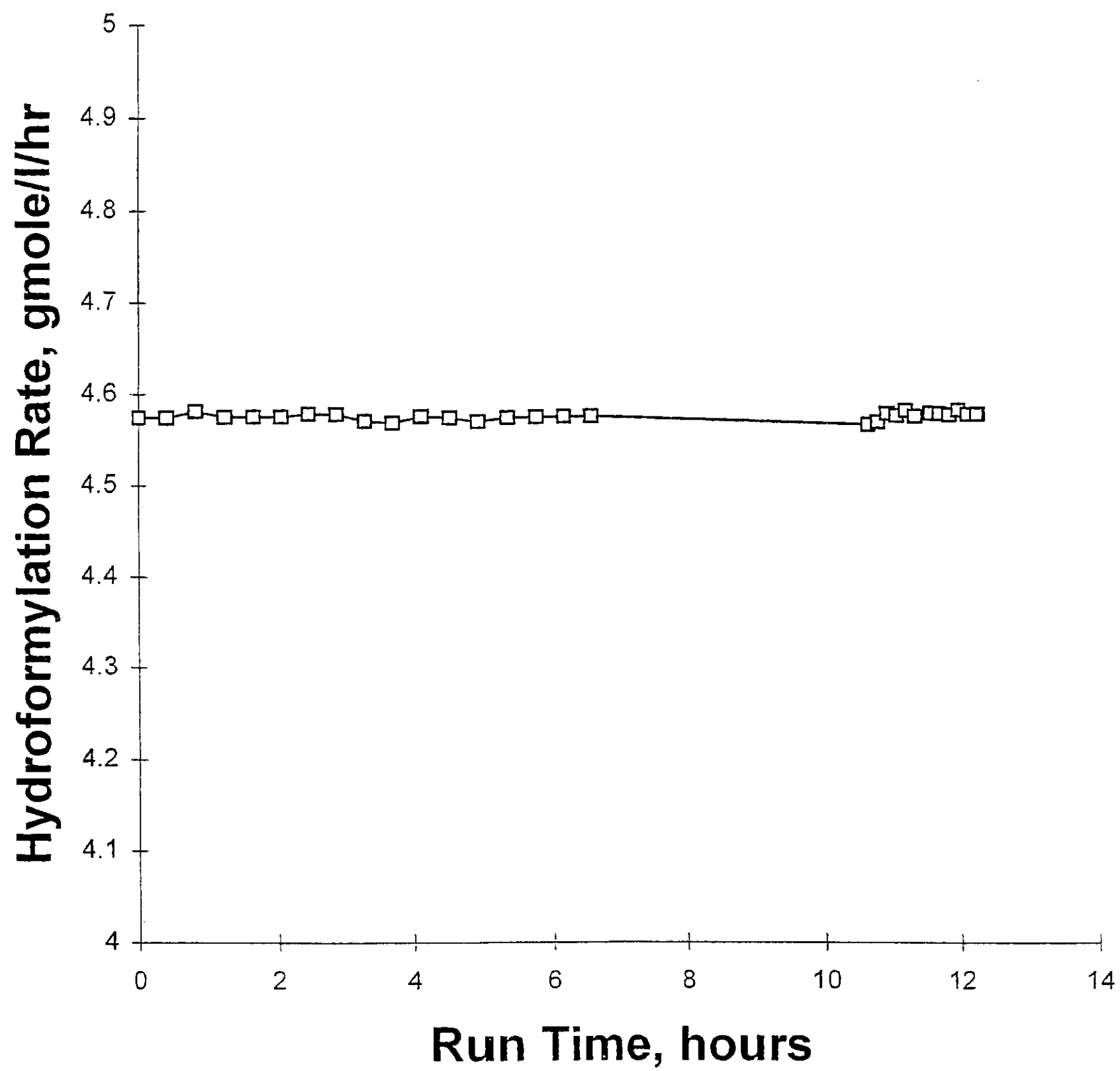


1. Impeller
2. Impeller shaft
3. Propylene feed line and feed flow control
4. Syngas feed line, sparger and feed flow controller
5. Vent flow line and vent flow control
6. Total pressure sensor
7. Exit line for product solution/catalyst to product recovery system
8. Feed line for catalyst returned from product recovery system
12. Carbon monoxide feed controller for total reactor pressure control


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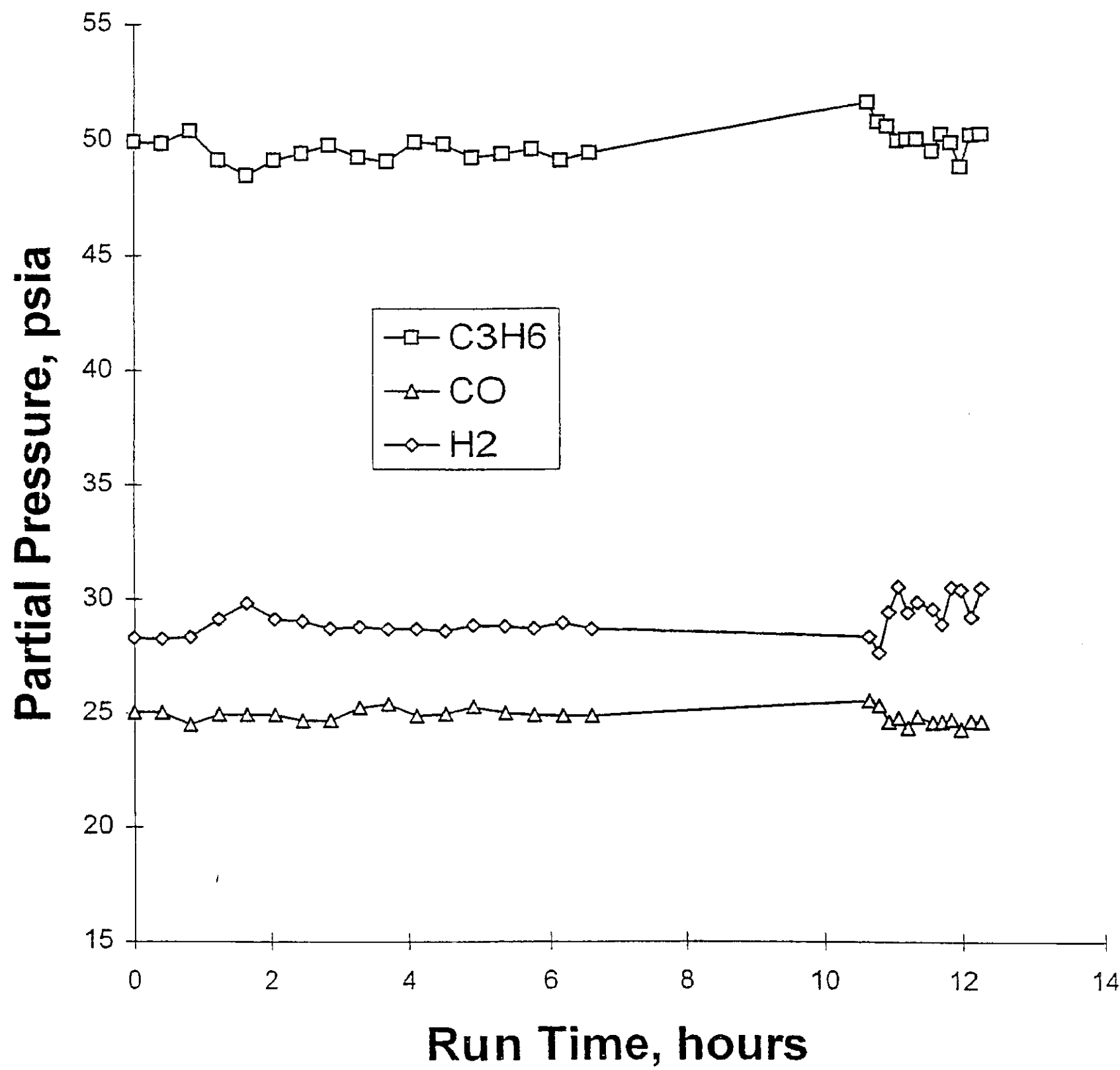
FIG 14





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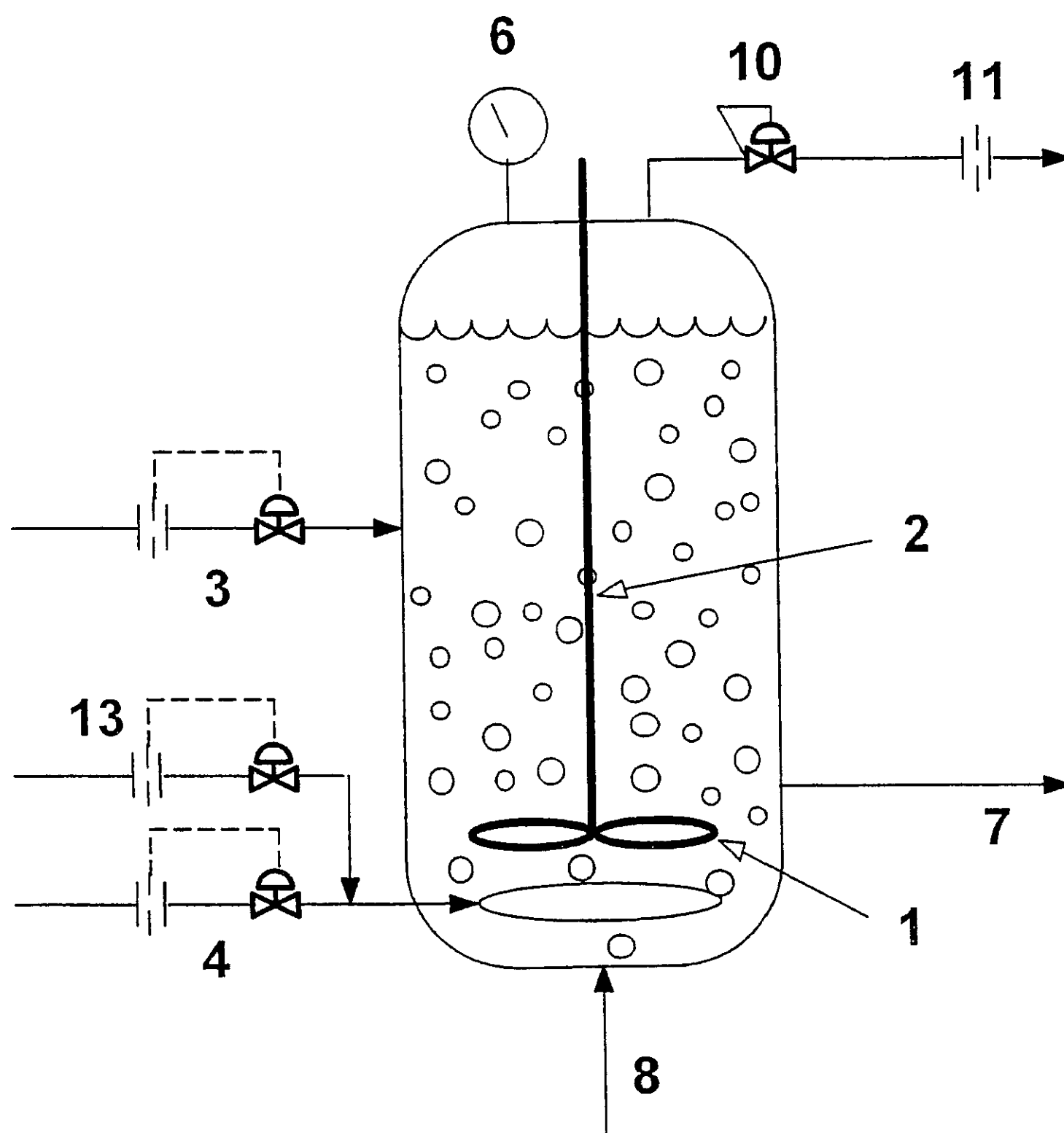
FIG 15




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FIG 16



1. Impeller
2. Impeller shaft
3. Propylene feed line and feed flow control
4. Syngas feed line, sparger and feed flow controller
6. Total pressure sensor
7. Exit line for product solution/catalyst to product recovery system
8. Feed line for catalyst returned from product recovery system
10. Reactor total pressure control
11. Reactor vent flow sensor
13. Carbon monoxide feed flow controller

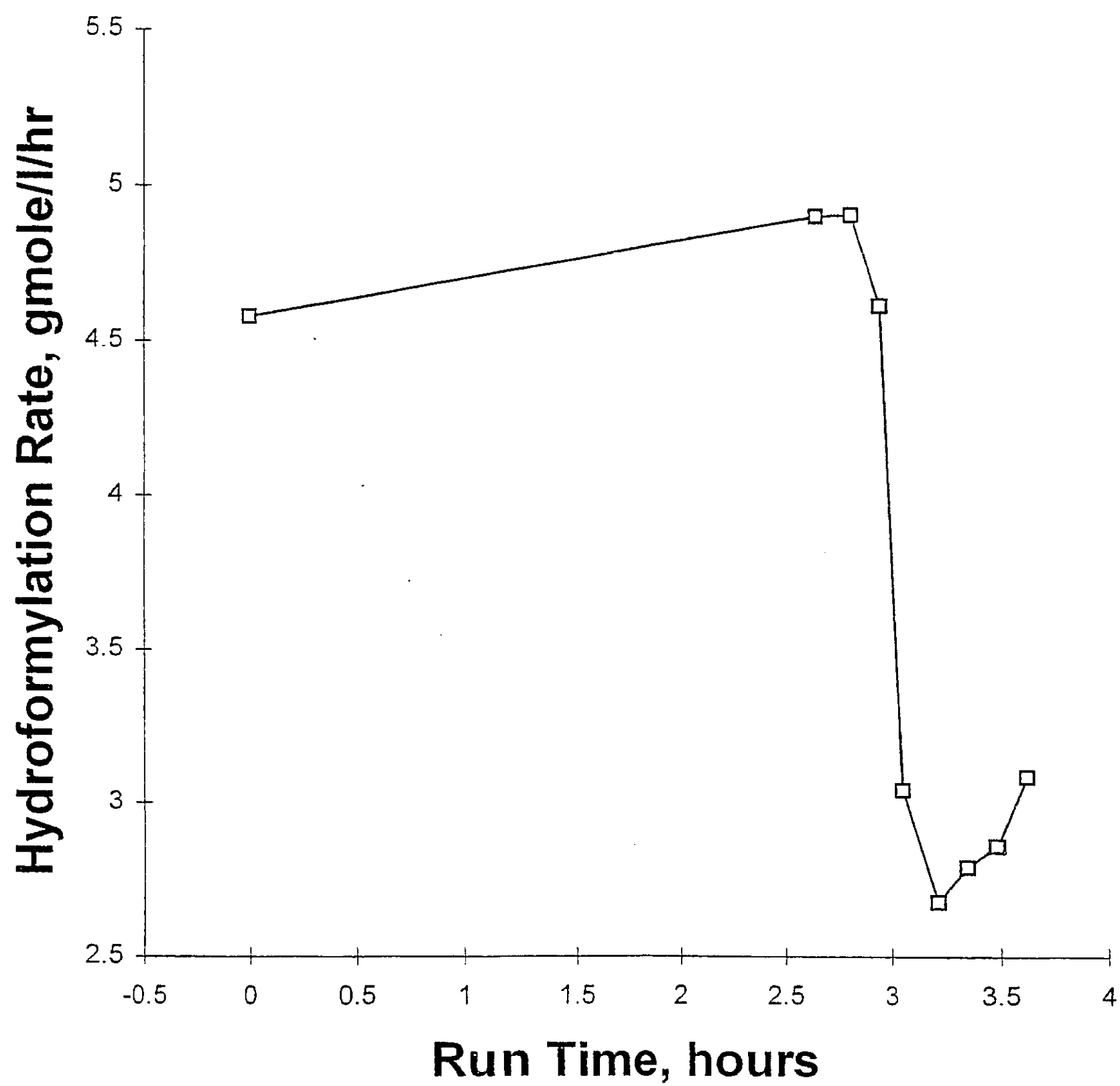
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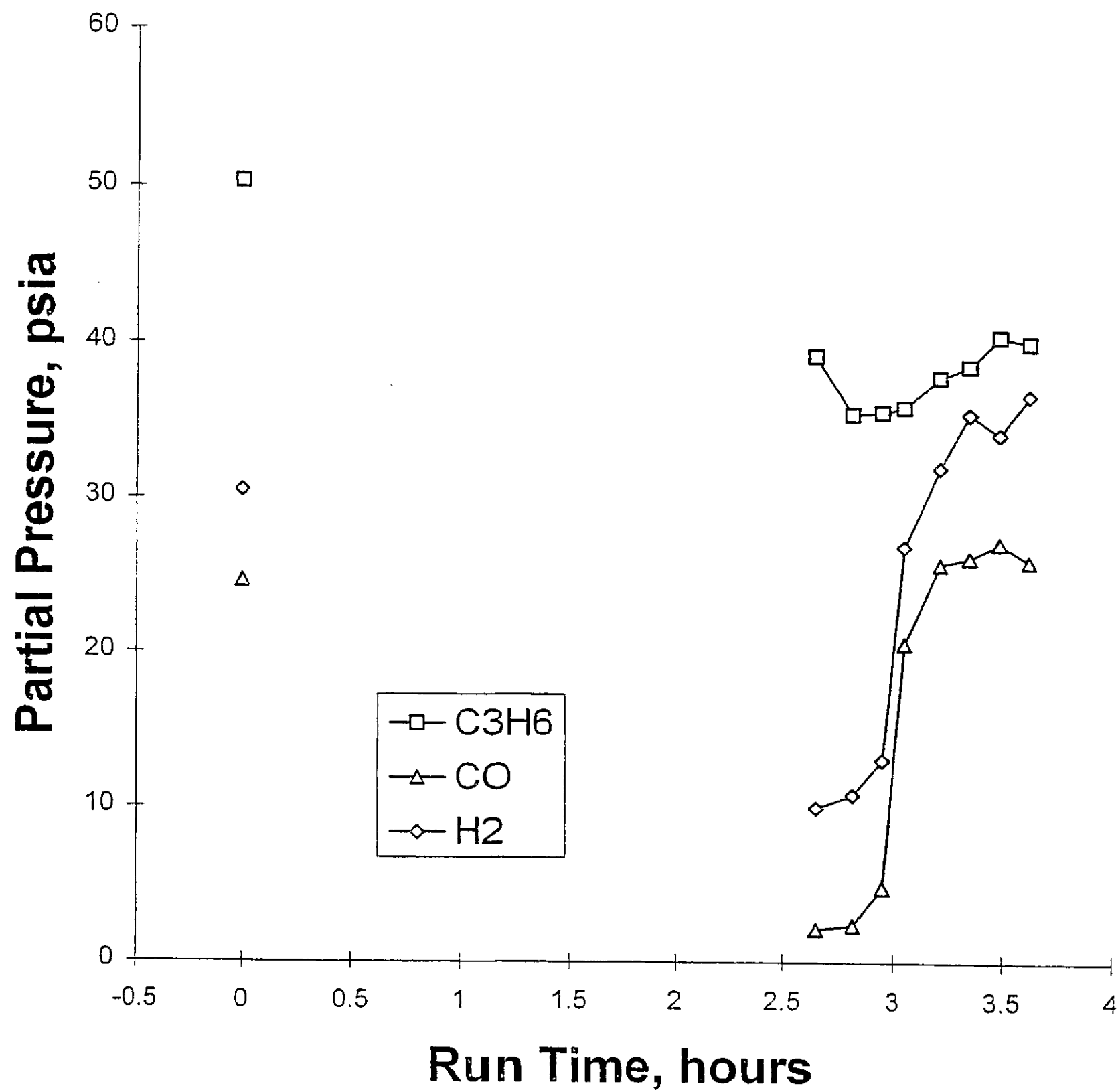
FIG 17



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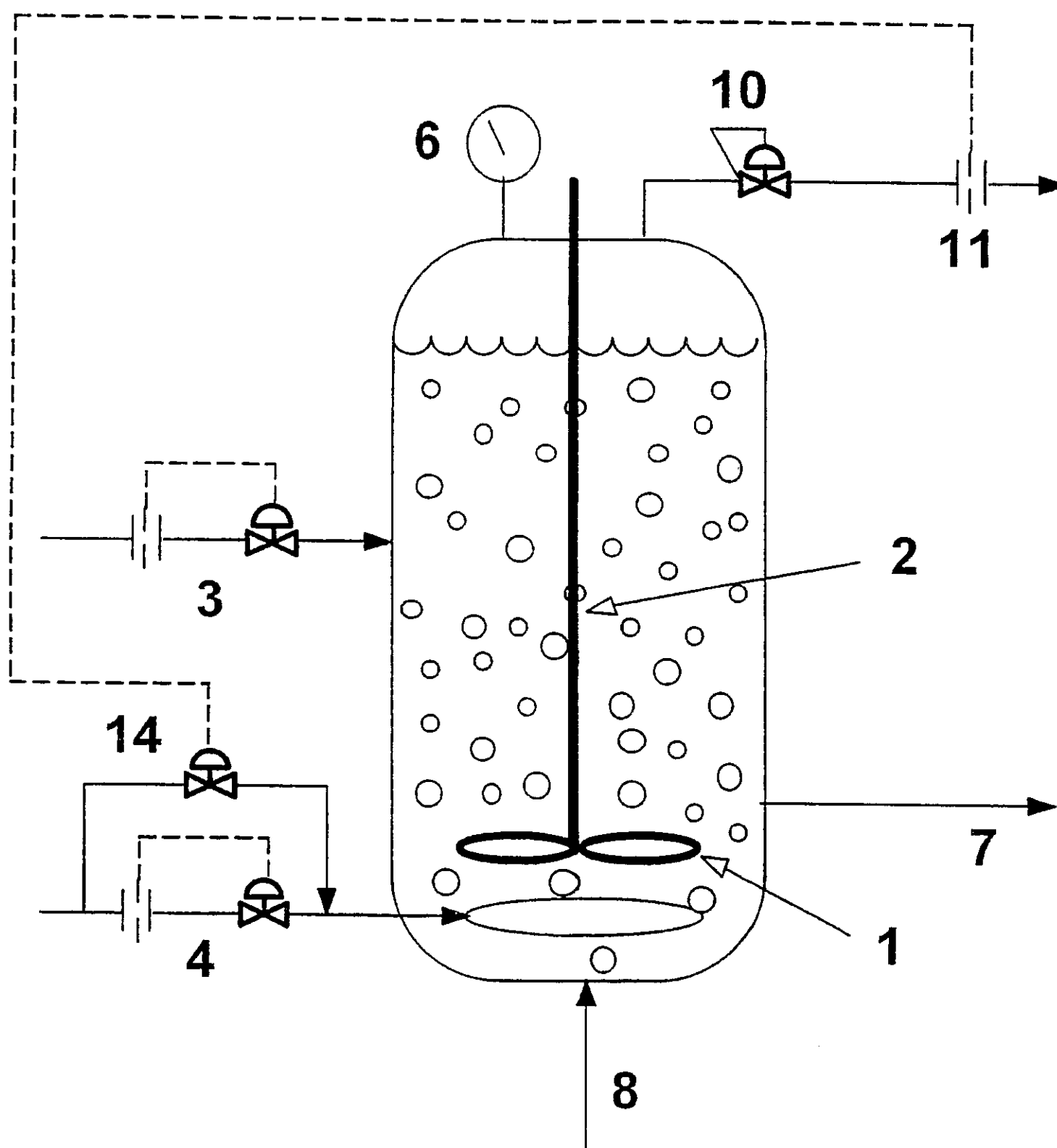
FIG 18




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FIG 19



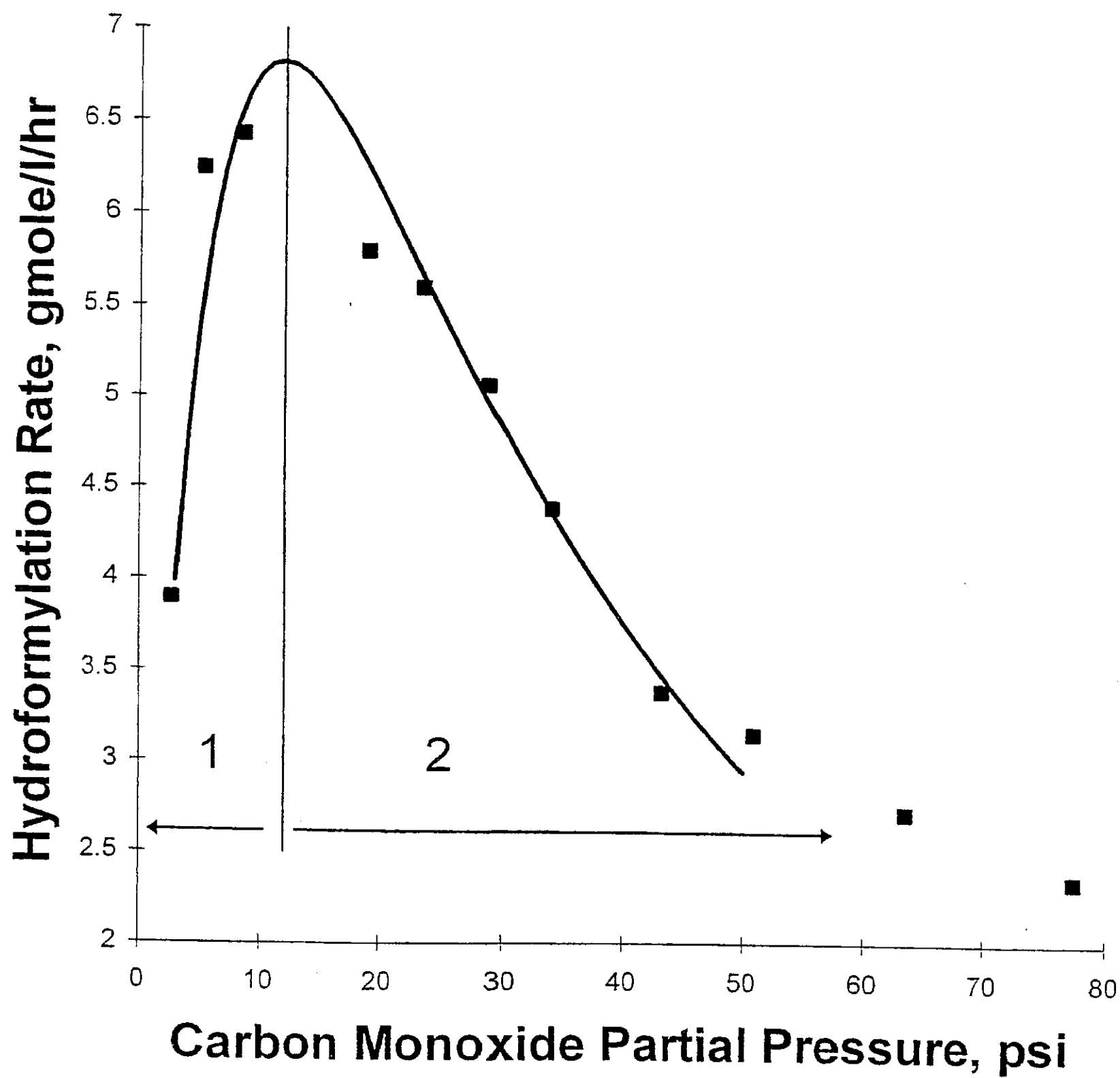
1. Impeller
2. Impeller shaft
3. Propylene feed line and feed flow control
4. Syngas feed line, sparger and feed flow controller
6. Total pressure sensor
7. Exit line for product solution/catalyst to product recovery system
8. Feed line for catalyst returned from product recovery system
10. Reactor total pressure control
11. Reactor vent flow sensor
14. Syngas feed line to control total reactor vent flow rate

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FIG 20



1. Positive order region
2. Negative or inverse order region

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