



(72) ROY, Surajit, CA

(72) PRUDEN, Barry B., CA

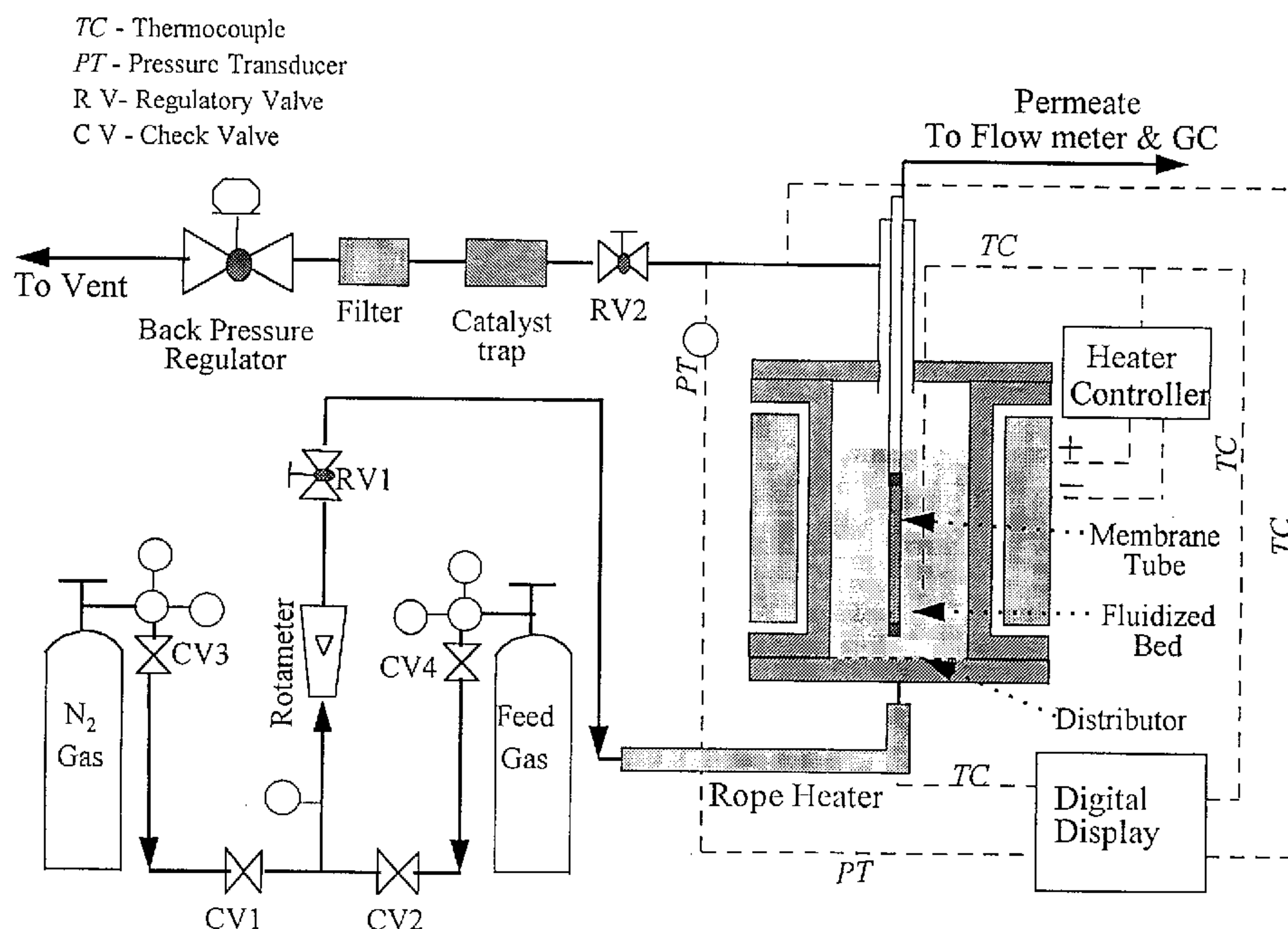
(72) BUXBAUM, Robert E., US

(71) UNIVERSITY TECHNOLOGIES INTERNATIONAL INC., CA

(51) Int.Cl.⁶ B01D 53/22

(54) **MEMBRANES TUBULAIRES POUR HAUT DEBIT A
REVETEMENT DE PALLADIUM**

(54) **PALLADIUM COATED HIGH-FLUX TUBULAR MEMBRANES**



(57) A high-flux tubular membrane for hydrogen separation in a fluidized bed membrane reactor at high temperatures and high pressures comprises a metal tube reinforced internally with a coil spring. The metal may preferably be palladium, niobium, tantalum, zirconium or vanadium or suitable alloys of such metals. If the metal is not palladium, the metal is preferably coated with palladium. The coil spring preferably is fashioned of stainless steel and fits tightly within the bore of the tubular membrane. The tubular membrane may be a straight tube or may be U-shaped.

ABSTRACT

A high-flux tubular membrane for hydrogen separation in a fluidized bed membrane reactor at high temperatures and high pressures comprises a metal tube reinforced internally with a coil spring. The metal may preferably be palladium, niobium, tantalum, zirconium or vanadium or suitable alloys of such metals. If the metal is not palladium, the metal is preferably coated with palladium. The coil spring preferably is fashioned of stainless steel and fits tightly within the bore of the tubular membrane. The tubular membrane may be a straight tube or may be U-shaped.

PALLADIUM COATED HIGH-FLUX TUBULAR MEMBRANES

FIELD OF THE INVENTION

5

The present invention relates to palladium coated high-flux tubular membranes for hydrogen separation.

BACKGROUND OF THE INVENTION

10

Membrane reactors may utilize membranes for product separation or purification in conjunction with chemical reactions. Such reactors are particular suited for reactions which are equilibrium limited, as significant enhancement over the equilibrium conversion may be achieved by selectively removing one or more reaction products through the membrane wall. It is well-known to use palladium and its alloys to form such membranes due to their high permeability, chemical compatibility with many hydrocarbon-containing gas streams and infinite hydrogen selectivity. Known palladium based membrane applications include steam reforming of methane, water gas shift, dehydrogenation of various compounds including hydrocarbons such as cyclohexane, ethylbenzene, ethane, propane and butane.

20

Theoretically, there are several metals such as niobium, tantalum, zirconium and vanadium which are more permeable to hydrogen than palladium. These metals are also much stronger than palladium. Therefore, even thin-walled membranes of these metals may provide the necessary thermal and mechanical strength to withstand high temperatures and differential pressures. Furthermore, as flux is inversely proportional to membrane thickness, it is possible that thin-walled membranes of these metals have theoretical fluxes that are orders of magnitude greater than that of palladium alone.

25

However, these metals are not used for hydrogen separation because the measured transport fluxes for these metals are much less than those predicted. It is believed that these metals have an inherent surface resistance or have a tightly held oxide film which

30

impedes absorption. It is known to provide a very thin layer of palladium coated on the surface. This palladium coat serves two purposes - it catalyzes the molecular hydrogen dissociation and recombination reactions on the surface, and decreases the transport barrier for hydrogen atom absorption into the refractory metal. In addition, the palladium layer protects the refractory metal from oxidation. These palladium coated refractory metal membranes show the greatest promise for membrane separators for hydrogen separation.

Hydrogen flux through a composite membrane is inversely proportional to membrane thickness and increases with pressure differential. Therefore, there is a need in the art for a thin-walled composite membrane which is strong enough to withstand very high pressure differentials at the high temperatures which may be encountered in membrane hydrogen separation reactors.

SUMMARY OF THE INVENTION

In one aspect of the invention and in general terms, the invention comprises a composite tubular membrane having an outer surface and an inner surface defining a cylindrical bore, said membrane comprising:

- a) a refractory metal chosen from the group of niobium, tantalum or vanadium;
- b) a palladium coating on both the inner and outer surfaces; and
- c) structural support means within the bore.

The structural support means preferably comprises a stainless steel spring closely engaging the inner surface of the tubular membrane. It is preferable if the spring is compactly coiled within the bore. Further, it is preferable if the thickness of the palladium coating is greater than about 3.0 μm and more preferably greater than about 4.0 μm .

The tubular membrane may be a straight tube or may be U-shaped. In either embodiment, one end of the membrane is sealed and the other end is adapted to connect with a separation reactor.

5 BRIEF DESCRIPTION OF THE DRAWINGS

The invention may be described with reference to the following the drawings:

Figure 1 - Permeation and abrasion test assembly.

10

Figure 1a - Cross-sectional view of a tubular membrane of the present invention.

Figure 1b - An alternative tubular membrane of the present invention.

15

Figure 1c - Is a U-shaped tubular membrane of the present invention.

Figure 2 - Effect of superficial velocity on permeation.

20

Figure 3 - Effect of temperature on permeation rate with pressure as a parameter.

Figure 4 - Permeability variation with temperature for different membrane tubes.

25

Figure 5 - Effect of hydrogen partial pressure on permeate flux.

Figure 6 - Effect of palladium coating thickness on overall transport temperatures.

30

Figure 7 - Effect of hydrogen partial pressure on molar flux at different temperatures.

Figure 8 - Variation of hydrogen flux with partial pressure for different feed mixtures.

Figure 9 - Variation of permeation rate with partial pressure for different membranes.

Figure 10 - Permeability variation with temperature for different membranes.

DETAILED DESCRIPTION OF THE INVENTION

It is generally accepted that hydrogen permeates through dense metallic membranes by a "solution-diffusion" mechanism. The essential steps were described by Barrer (1951) and Athayde et al. (1994). The flux of hydrogen through a metal membrane can be estimated by (Collins and Way, 1993; Uemiya et al., 1991b; Hurlbert and Konecny, 1961):

$$J_{H_2} = P_M \left(\frac{P^{H_{2h}} - P^{H_{2l}}}{l} \right) \quad (1)$$

The relationship can be derived from Fick's first law. According to Fick's law, the flux of hydrogen atoms through a homogeneous metal phase can be calculated from:

$$J_H = D_M \left(\frac{C_{Hh} - C_{Hl}}{l} \right) \quad (2)$$

When diffusion through the metal is the rate limiting step (i.e. dissolved hydrogen atoms are in rapid equilibrium with the hydrogen molecules in the gas phase) and hydrogen atoms from

an ideal solution in the metal, C_H is related to the partial pressure of hydrogen in equilibrium with the metal via Sieverts thermodynamic equation:

$$C_H = K_S (P^{0.5}) \quad (3)$$

Combining Equations 1 and 2, the value obtained for n is equal to 0.5 (Buxbaum and Kinney, 1996; Buxbaum and Marker, 1993; Collins and Way, 1993; Hurlbert and Konecny, 1961).

If the surface adsorption of hydrogen on palladium is the rate determining step, the concentration of hydrogen at the interface of the membrane can be written as (Wijmans and Baker, 1995):

$$C_{Hh} = K_R P_{H_2}$$

Combining Equations 2 and 4, the value obtained for n is equal to 1.0 (Wijmans and Baker, 1995).

When the rate of permeation is governed by both surface adsorption of hydrogen molecules and diffusion of hydrogen atoms through the bulk of the metal, the value of ' n ' is between 0.5 to 1.0 (Hurlbert and Konecny, 1961; Collins and Way, 1993; Yan et al., 1994).

Deviation from ideal solution behavior (Sieverts law, Equation 3) also influences the value of the pressure exponent ' n '. At low concentrations, hydrogen atoms form an ideal solution in the metal and there is no interaction between the hydrogen atoms as they diffuse through the metal. When the partial pressure of hydrogen in the gas phase is high, the atomic hydrogen concentration in the metal also increases and the adsorbed

hydrogen atoms attract each other. Therefore at high hydrogen partial pressures, the atomic hydrogen concentration in the metal (C_H) is more than the value predicted by Sieverts Law (Equation 3) (Buxbaum and Kinney, 1996). If K_S is taken as constant, this effect increases the value of the pressure exponent from 0.5 in Equation 3. The deviation from ideal behavior (i.e. deviation from $n=0.5$ behavior) is more pronounced in metals that form hydrides (e.g. palladium) with hydrogen atoms (Le Claire, 1983). In these metals, the deviation is encountered even at comparatively low pressures.

Another factor which influences with value of 'n' is the leakage of gas through metal film or membrane seals (Collins and Way, 1993). Since flow through any leak is hydrodynamic, the flow rate depends on the absolute pressure difference and not on the difference in hydrogen partial pressures.

The value of 'n' may also depend on temperature since it is affected by the Sieverts constant (K_S), diffusivity (D_M) and ratio of the rates of surface processes and bulk diffusion which all depend on temperature.

Hydrogen permeation experiments conducted with palladium have yielded n values of 0.5 (Buxbaum and Kinney, 1996; Buxbaum and Marker, 1993; Uemiya et al. 1991b; Holleck, 1970), 0.68 (Hurlbert and Konecny, 1961), 0.76 (Uemiya et al., 1991a), 0.80 (De Rosset, 1960), 0.53-0.62 (Collins and Way, 1993) and 1.0 (Yan et al., 1994). All these experiments were conducted at temperatures ranging from 340°C to 460°C and hydrogen feed pressures ranging from 101 to 4926 kPa.

Since both the diffusivity and Sieverts constant vary in an Arrhenius manner with temperature, the permeation constant can be expressed in terms of a pre-exponential factor, P_{MO} , and an activation energy, E_p , by:

(5)

$$P_M = \frac{D_M K_S}{2} = P_{MO} \exp\left(-\frac{E_p}{R_g T}\right) \quad (5)$$

Two other quantities, "permeance" and "total resistance to transport" can be derived from Equation 1. "Permeance", Φ , is defined as the flux divided by the pressure driving force:

$$\Phi = \frac{J_{H_2}}{P^{H_2} - P^{H_2}} = \frac{P_M}{t} \quad (6)$$

The inverse of permeance is the "total resistance to transport",

$$R_{tot} = \frac{1}{\Phi} = \frac{(P^{H_2} - P^{H_2})}{J_{H_2}} = \frac{t}{P_M} \quad (7)$$

For the High-flux membranes used for this study, the total resistance to transport will be the sum of the resistance offered by the palladium coating, and the constant resistance (R_c) which accounts for the resistance offered by the substrate plus interfacial resistances between the coatings and the substrate:

$$R_{tot} = \frac{t}{P_M} + R_c \quad (8)$$

The diffusion rates reported by different authors for palladium membranes differ by orders of magnitude. For example, the rates reported for a 50 μm palladium membrane at 300°C by Jost and Widman (1940), Silberg and Bachman (1958), Barrer (1940) and Hurlbert and Konecny (1961) are in the ratio of 0.005:01:0.3:1. Also the reported activation energy (E_p) for permeation of hydrogen through palladium differs considerably. For example, Holleck (1970) reported an activation energy (E_p) of 43.97 ± 0.42 kJ/mol whereas Katsuta et al. (1979) determined E_p to be 20.5 ± 1.4 kJ/mol.

As the data given by others has variability which is probably a result of the purity of the palladium and the state of the palladium surface, the permeability pre-exponential factor (P_{MO}), the activation energy (E_p) and the pressure exponent (n) were determined for our membranes from experimentally obtained permeation rates. At a particular temperature, the effective permeability of the high flux membrane tube, P_M , and pressure exponent, n , were determined from nonlinear regression analysis of Equation 1. From experiments performed at different temperatures, the permeation pre-exponential factor and the activation energy were estimated using linear regression analysis of the following Equation:

$$\ln P_M - \ln P_{MO} = \frac{E_p}{R_g T} \quad (9)$$

The total resistance was determined from Equation 7. The resistance and permeability of the palladium coating and the constant resistance were determined by linear regression analysis of Equation 8.

Apparatus and procedure

Permeabilities and selectivities of membrane tubes were studied using the permeation and abrasion test assembly shown in Figure 1. The permeation and abrasion unit consisted of a cylindrical vessel flanged at both ends with a distributor plate at the bottom. As the feed gas (mixture of N_2 and H_2) flowed up the catalyst bed, a small fraction of hydrogen permeated through the membrane and the retentate exited from the top of the vessel. The flow rate of the permeate was measured by water displacement method and its composition was analyzed at regular intervals by a Shimadzu GC-8A IT Chromatograph. At each temperature and pressure, steady state was assumed when two successive flow rate measurements were within 4%. The pressure in the permeation unit was maintained at the set point by a back pressure regulator, whereas the pressure at the permeate side was always atmospheric. The membrane tubes used for permeation studies were 6.0 to 9.0 cm long.

Sufficient reforming catalyst, which is essentially Ni supported on alumina (Al_2O_3) was used to ensure that all of the membrane tube remain submerged in the fluidized bed. The substrate metal (alloy) thickness of all the high flux tubes was $76.1\ \mu\text{m}$ and the palladium coating varied from approximately 3 to $9\ \mu\text{m}$ on the inside and outside of the tubes. The top ends of the tubes were brazed to 316 SS (stainless steel) tubes of slightly larger diameter using a commercially available high temperature braze UTP 6 (Bohler UTP Welding Canada, Ltd.) and the bottom ends were sealed using 316 SS plugs brazed with UTP 6. The 316 SS tube was sealed to the permeation unit by Swagelok fittings. The retentate gas passed through a catalyst bed and the permeation unit were preheated to 400°C with nitrogen flow. This was performed to prevent damage to the palladium layer, because pinholes or cracks could be formed by phase transformation of palladium hydride from the α to the β -phase on exposure to hydrogen at temperatures below 300°C .

For the first set of experiments, each of the two membrane tubes had an outside diameter of 1.98 mm and a substrate metal alloy thickness of $38\ \mu\text{m}$. One end of each membrane tube was first brazed to a 3.34 mm ID 316 SS tube which was then brazed to a 4.93 mm ID 316 SS tube while the other end was plugged by brazing. The brazed tubes, supplied by REB Research, had palladium coating of 4 and $6\ \mu\text{m}$ on both the inside and outside. Both of the tubes collapsed and resembled thin sheets at an operating temperature of 600°C . This collapse caused stress in the braze and a leak developed at the point where the membrane was brazed to the stainless steel tube. Normally these tubes have pressure in the inside, and the thickness was computed to more than contain the pressure at 700°C . However computations for tubes with pressure on the outside are approximate, as much depends on tubes being perfectly round.

New membranes with greater wall thickness ($64\ \mu\text{m}$) were used for a second set of experiments. The outside diameter of the membrane tubes were 1.98 mm and they were brazed to 3.18 mm OD 316 SS tubes. The tubes had a palladium coating thickness of 4.2 and $6.2\ \mu\text{m}$, respectively. These membrane tubes were also crushed into the shape of thin sheets, although there was no leak (i.e. no nitrogen peak was detected in the permeate gas) as

the brazing remained intact. Surprisingly, the permeate continued to flow through the continuous channels of the crushed tube.

Results and discussion

5

From the initial experiments it was clear that the alloy tubes were unable to maintain their mechanical structure at high temperature. It was decided to reinforce the membranes by inserting springs inside the tubes. Two spring reinforced membranes were tested for permeation and high temperature and pressure resistance. The membrane tubes had an outside diameter of 3.18 mm and a substrate metal thickness of 76 μm . Each tube was first brazed to a 3.34 mm ID tube which was subsequently brazed to another 1.75 mm ID SS tube. Both of the tubes started leaking at approximately 600°C and 1378 kPa. The leak occurred due to the inability of the braze (performed by REB Research using Braze 505) to withstand this high temperature. But the spring reinforcement prevented the tubes from collapsing. The brazing of all the tubes tested afterwards was carried out using a high temperature braze called UTP 6 (49.0% Cu, 10.6% Ni, 1.0% Ag and the balance Zn & other traces).

15

20

25

The High-flux membrane tubes used for the next set of experiments had outside diameters of 3.18 mm and substrate metal thickness of 76 μm . The palladium coating thickness of these tubes was 1.94, 4.05, 6.33 and 7.8 μm . Because of the very thin palladium layer, it was not possible to braze the 1.94 μm membrane to a stainless steel tube, so it was not used. Permeation studies were performed with the 6.33 and 4.05 μm membranes at different temperatures and differential pressure. For the 6.33 μm membrane, nitrogen was detected in the permeating gas at 625°C and 1330.3 kPa. Since, the spring inside the tube was not compact, the high outside pressure at this high temperature caused both the spring and the tube to collapse. For the same reason, the 4.05 μm tube collapsed at 1330.3 kPa and 600°C.

The following conclusions were drawn from all the experimentation up to this point.

i) Spring reinforcement is preferable to provide strength at these high temperatures and differential pressures. Moreover, the spring needs to be packed compactly although it may decrease the surface area for desorption.

ii) Brazing becomes very difficult if the palladium coating thickness is very low. The coating should be more than $3.0\ \mu\text{m}$ and preferably above $4.0\ \mu\text{m}$.

iii) UTP 6 can withstand the high temperatures and differential pressures used in the present investigation. For proper brazing, dust, oil and other surface contaminants have to be removed from the stainless steel surface.

PERMEATION CHARACTERISTICS

All the tubes tested for permeation characteristics had an outside diameter of 1.98 mm and substrate metal thickness of $76\ \mu\text{m}$. One end of each tube was plugged with brazing and the other end was brazed to a 3.34 mm ID 316 SS tube.

Figure 2 shows the effect of change in superficial velocity on the permeabilities of pure palladium and High-flux membrane tubes. Each data point in this figure and all the figures used afterwards represent the average of three readings. The maximum percentage deviation from the mean value was $\pm 5\%$. From the results of Figure 2, it can be concluded that the permeation rate was independent of superficial velocity i.e. there is no diffusional resistance in the catalyst bed.

Figure 3 and 4 show the temperature effects on the flux and permeabilities of different High-flux membrane tubes. Although, there is considerable scatter in the data of Figure 3, the trend follows Arrhenius behavior. Experimentally, the scatter might be due to

difficulties in controlling the temperature and pressure inside the permeation unit. The temperature varied by as much as 10°C from the mean whereas the pressure varied from the mean value by ± 35 kPa.

The pre-exponential factors (P_{MO}) in Equation 9 for the 3.8, 5.4 and 8.25 μm membranes were determined to be 9.95×10^{-9} and 5.48×10^{-9} $\text{mol}/(\text{m.s.Pa}^{0.72})$, respectively and the corresponding activation energies (E_p) were 12.7, 11.5 and 9.6 kJ/mol. The above mentioned P_{MO} and E_p values account for the combined effect of the palladium coating and the alloy substrate. Activation energy is positive (i.e. permeation increases with increasing temperature) for palladium while it is negative for niobium and tantalum. As diffusion through the palladium coating is the rate limiting step, it dominates the overall activation energy of the High-flux membrane. The E_p for pure palladium is 10.5 ± 1.4 kJ/mol (Katsuta et al., 1979). For High-flux membranes this value is clearly reduced because of the opposing effect of exothermic absorption in the substrate alloy.

The effect of hydrogen partial pressure on the permeation flux for different membrane tubes is shown in Figure 5. The pressure exponent ' $n = 0.72$ ' was determined from nonlinear regression analysis using the combined permeation data from three different membrane tubes in Equation 1. One of the reasons for the high value of n is that all the experiments were performed at high hydrogen concentration (40% H_2 in the feed), which causes deviations from ideal solution behavior and thus Sievert's law.

The reciprocal of the slopes of the best fit lines in Figure 5 are the transport resistances of different membrane tubes at 600°C. These resistances are plotted against the palladium coating thickness in Figure 6. The intercept of the line with the resistance axis, which was about $48700 \text{ m}^2.\text{s.Pa}^{0.72}/\text{mol}$, represents the constant resistance offered by the substrate alloy plus the metal-metal interfaces. The slope of the best fit line represents the resistance offered per 1 μm palladium coating and was about $1450 \text{ m}^2.\text{s.Pa}^{0.72}/\text{mol}$. For a single membrane tube, the variation of permeation rate with hydrogen partial pressure at three different temperatures is plotted in Figure 7. From this plot it can be concluded that for the

temperature range 400 to 600°C, the pressure exponent 0.72 satisfactorily describes the permeation characteristic of the membrane.

In most of the runs the composition of the feed mixture was 40% H₂ and 60% N₂. The high concentration of nitrogen was used so that even a small leak could be detected by analyzing the permeate. Experiments were also conducted using a 27.1% CH₄ and 72.9% H₂ feed mixture. Figure 8 shows the variation of hydrogen flux with pressure for the two feed gas mixtures. The slopes of the best fit straight lines for the two sets of data are almost equal which means that the permeability is independent of the concentration of hydrogen and the choice of the non-permeating component.

For comparison purposes, a permeation study was performed using palladium tubes supplied by Johnson Matthey Ltd. which were used by Adris (1994). Figure 9 shows that the permeation rate was more than three times higher for the High-flux tubes. The permeability variation with temperature for the two membrane tubes is plotted in Figure 10. The permeation activation energies (E_p), calculated from the slopes of the lines, were 9.580 kJ/mol for the High-flux tube and 20.559 kJ/mol for the palladium tube. The E_p value for the palladium tube was close to the value (20.5 ± 1.4 kJ/mol) reported by Katsuta et al. (1979).

The brazing with UTP 6 was not perfect as it failed in some occasions below a temperature of 650°C. As a result of this uncertainty, a different method was used to join the membrane tube and the stainless steel tube. A Conax™ PG gland with Grafoil sealant was used to connect the membrane tube to the 316 SS tube. A 3.18 mm OD SS tube was first machined to decrease its outer diameter so that it fit snugly inside the spring reinforced membrane tube. A Grafoil sealant was crushed on to the contacting/overlapping surface of the two tubes. Membrane tubes with Conax™ fitting at the top and braze at the bottom were tested successfully (without any leak) up to a temperature of 670°C and a differential pressure of 1410 kPa.

Conclusions

The spring reinforced High-flux membrane tubes were tested for permeation over the temperature range of 400-700°C and at differential pressures up to 1480 kPa. This is a significant improvement as this type of membranes were earlier tested only up to a temperature of 425° and a differential pressure of 110.3 kPa. Also the abrasion resistance of the palladium coating was tested in the fluidized bed of catalyst particles and found to be satisfactory. Due to their stability at high temperatures, differential pressures and a fluidized bed environment, the spring reinforced High-flux membrane tubes are the preferred membrane in membrane reactors including fluidized bed membrane reformers which require operation at relatively high temperatures and transmembrane pressure difference.

The dimensions of the tubular membranes may be scaled up to accomodate existing fluidized bed membrane reformers as is well known in the art. However, the thickness of the palladium coating should remain the same. Such tubular membranes are well suited to large scale hydrogen extractors using well-known shell and tube heat exchanger designs.

As shown in Figure 1a and 1b, a tubular membrane (10) is fitted with an internal coil spring (12) which reinforces the membrane (10) and resists deformation of the membrane under high transmembrane pressure differentials. The coil spring (12) is preferably made of stainless steel. As shown in Figure 1c, the tubular membrane (10) may be bent into a U-shaped membrane to increase membrane surface area in a reactor with limited permeate discharge connectors. The internal spring (12) is not shown in Figure 1c.

In either the straight or U-shaped membranes, one end (14) is plugged while the other end (16) is open as a permeate discharge opening. The open end (16) may be connected to a stainless steel connecting tube (not shown) by brazing as described above or more preferably to Cornax™ stainless steel connectors available from Cornax Buffalo Inc.,

Buffalo, New York with an appropriate sealant such as Grafoyl™ available from Union Carbide.

5 In one application, the U-shaped tubular membranes are approximately 45 cm in height (90 cm in total length), have an outside diameter of approximately 3.2 mm, a wall thickness of approximately 76 μm and a palladium coating thickness of approximately 4 μm . These specific dimensions are not critical to the invention but are exemplary of a preferred embodiment.

10 As will be apparent to those skilled in the art, various modifications, adaptations and variations of the foregoing specific disclosure can be made without departing from the teachings of the present invention.

Nomenclature

C_{Hh}	= concentration of hydrogen atoms at the high pressure side, mol/m ³
C_{Hl}	= concentration of hydrogen atoms at the low pressure side, mol/m ³
D_M	= diffusivity of atomic hydrogen, m ² /sec
E_p	= activation energy for permeation, J/mol
J_H	= flux of hydrogen atoms, mol/(m ² .sec)
J_{H2}	= molar flux of hydrogen, mol/(m ² .sec)
K_R	= sorption coefficient for hydrogen, mol/(m ³ .Pa)
K_S	= Sieverts constant, mols of atomic hydrogen/(m ³ .Pa ^{0.5})
P_{H2h}	= partial pressure of hydrogen in the feed or high pressure side, Pa
P_{H2l}	= partial pressure of hydrogen in the permeate or low pressure side, Pa
P_M	= effective permeability in terms of molar flow, mol/(m.sec.Pa ^{0.72})
P_{MO}	= permeation pre-exponential factor, mol/(m.sec.Pa ^{0.72})
R	= resistance to transport, m ² .sec.Pa ^{0.72} /mol
R_c	= constant resistance, m ² .sec.Pa ^{0.72} /mol
R_{tot}	= total transport resistance through composite metal membrane, m ² .sec.Pa ^{0.72} /mol
t	= thickness of the metal membrane, μm
t_{tot}	= total thickness of the membrane tube, μm
T	= temperature in the permeation unit, °C

Greek letter

ϕ	= permeance, mol/(m ² .sec.Pa ^{0.72})
--------	--

Superscript

n	= exponent showing the dependency of partial pressure of hydrogen on permeation rate
-----	--

Subscripts

h = feed or high pressure side
l = permeate or low pressure side
M = metal
H₂ = hydrogen

References

- Adris, A. M., "A Fluidized Bed Membrane Reactor for Steam Methane Reforming: Experimental Verification and Model Validation", Ph.D. Thesis, University of British Columbia, April 1994.
- Amano, M., M. Komaski and C. Nishimura, "Hydrogen Permeation Characteristics of Palladium Plated V-Ni Alloy Membranes", *J. Less-Common Met.*, 172-174, 727-731 (1991).
- Athayde, A. L., R. W. Baker and P. Nguyen, "Metal Composite Membranes for Hydrogen Separation", *J. Membr. Sci.*, 94, 299-311 (1994).
- Barrer, R. M., *Trans. Faraday Soc.*, 36, 1235 (1940).
- Barrer, R. M., "Diffusion in and through Solids", Cambridge University Press, London, 1951.
- Brown, C. C. and R. E. Buxbaum, "Kinetics of Hydrogen Absorption in Alpha Titanium", *Metal. Trans. A*, 19A, 1425-1427 (1988).
- Buxbaum, R. E. and P. C. Hsu, "Method for Plating Palladium", US Patent 5,149,420, 1992.
- Buxbaum, R. E. and A. B. Kinney, "Hydrogen Transport through Tubular Membranes of Palladium-Coated Tantalum and Niobium", *Ind. Eng. Chem. Res.*, 35(2), 530-537 (1996).
- Buxbaum, R. E. and T. L. Marker, "Hydrogen Transport through Non-Porous Membranes of Palladium-Coated Niobium, Tantalum and Vanadium", *J. Membr. Sci.*, 85, 29-38 (1993).
- Collins, J. P. and J. D. Way, "Preparation and Characterization of a Composite Palladium-Ceramic Membrane", *Ind. Eng. Chem. Res.*, 32, 3006-3013 (1993).
- De Rosset, A. J., "Diffusion of Hydrogen through Palladium Membranes", *Ind. Eng. Chem. Res.*, 52, 525-528 (1960).
- Hill, E. F., "Feasibility study: Removal of Tritium from Sodium During the MDEC Process by Oxidative Diffusion, Argonne West, DOE N707T1830035, 1982.
- Holleck, G. L., "Diffusion and Solubility of Hydrogen in Palladium and Palladium-Silver Alloys", *J. Phys. Chem.*, 74, 503-511 (1970).
- Hurlbert, R. C. and J. O. Konecny, "Diffusion of Hydrogen Through Palladium", *J. Chem. Phys.*, 34, 655-668 (1961).
- Jost, W. and A. Widman, *Z. Physik. Chem. (Leipzig)*, B45, 285 (1940).

- Katsuta, H., R. B. Farraro and R. B. McLellan, *Acta Met.*, 27, 1111-1114 (1979).
- Le Claire, A. D., "Permeation of Gases through Solids: I. Principles", *Diffusion and Defect Data*, 33, 1-66 (1983).
- Markides, A. C., M. A. Wright and D. N. Jewett, "Separation of Hydrogen by Permeation", US Patent 3,350,846, 1967.
- Sawatzki, A. and G. A. Ledoux, "The Use of Palladium to Remove Hydrogen from Zirconium", Presented at the 2nd International Congress on Hydrogen in Metals, Paris, France, 1977.
- Silberg, P. A. and C. H. Bachman, *J. Chem. Phys.*, 29, 777 (1958).
- Uemiya, S., N. Sato, H. Ando, Y. Kude, T. Matsuda and E. Kikuchi, "Separation of Hydrogen through Palladium Thin Film Supported on a Porous Glass Tube", *J. Membr. Sci.*, 56, 303-313 (1991a).
- Uemiya, S., T. Matsuda and E. Kikuchi, "Hydrogen Permeable Palladium-Silver Alloy Membrane Supported on Porous Ceramics", *J. Membr. Sci.*, 56, 315-325 (1991b).
- Wijmans, J. G. and R. W. Baker, "The Solution-Diffusion Model: A Review", *J. Membr. Sci.*, 107, 1-21 (1995).
- Yan, S., H. Maeda, K. Kusakabe and S. Morooka, "Thin Palladium Membrane Formed in Support Pores by Metal-Organic Chemical Vapor Deposition Method and Application to Hydrogen Separation", *Ind. Eng. Chem. Res.*, 33, 616-622 (1994).

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composite tubular membrane having an outer surface and an inner surface defining a cylindrical bore, said membrane comprising a metal chosen from the group of palladium, niobium, tantalum, vanadium or other metal suitable for hydrogen permation and structural support means within the bore.
2. The tubular membrane of claim 1 wherein the structural support means comprises a stainless steel spring engaging the inner surface of the tubular membrane.
3. The tubular membrane of claim 2 wherein said membrane comprises a metal which is not palladium, further comprising a thin palladium coating on both the inner and outer surfaces.
4. The tubular membrane of claim 3 wherein the thickness of the palladium coating is greater than about 3.0 μm .
5. The tubular membrane of claim 4 wherein the thickness of the palladium coating is greater than about 4.0 μm .
6. The tubular membrane of one of claims 1, 2, 3, 4 or 5 wherein the tubular membrane is U-shaped and one end thereof is sealed and the other end is adapted to connect with a separation reactor.

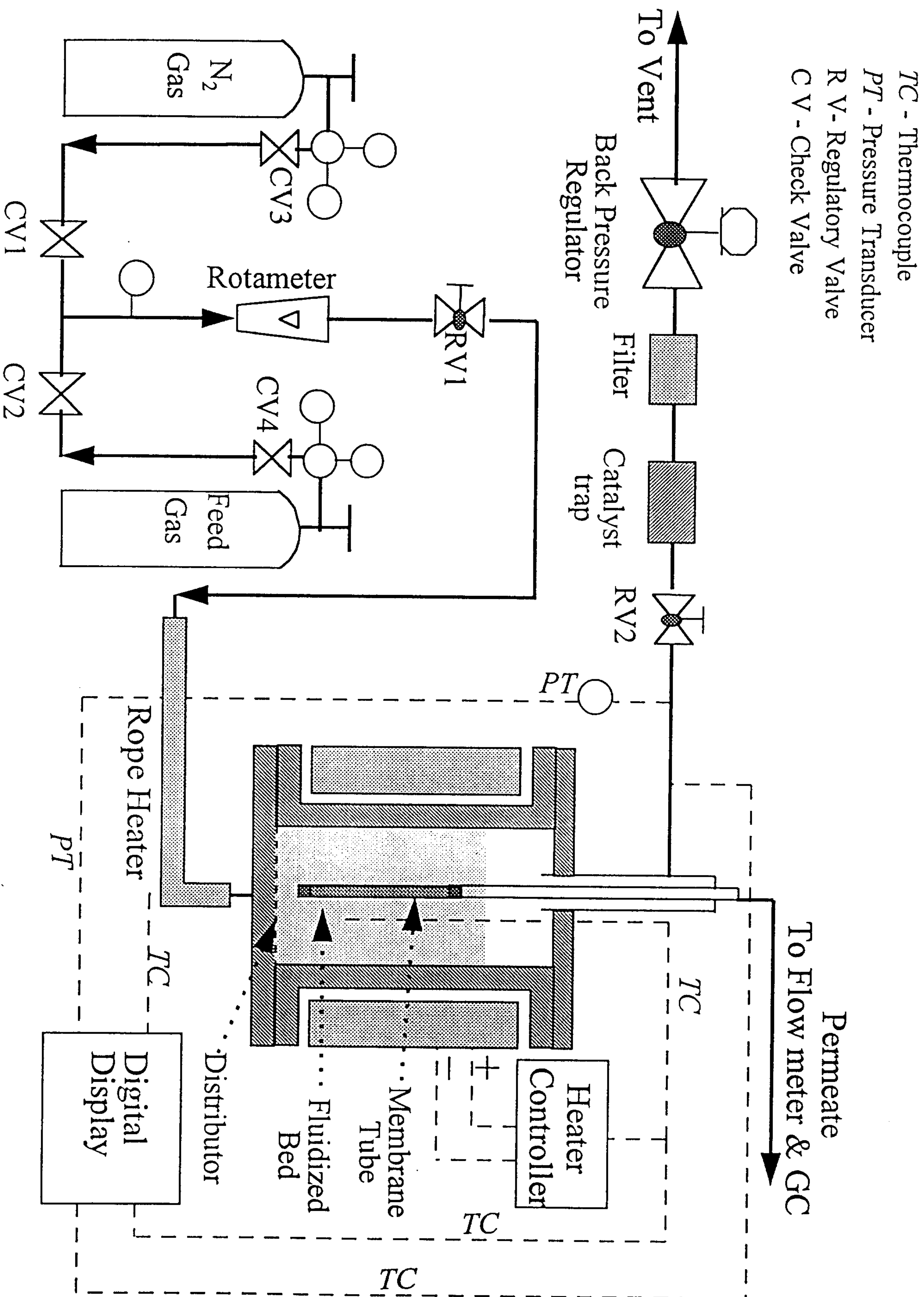


Figure 1

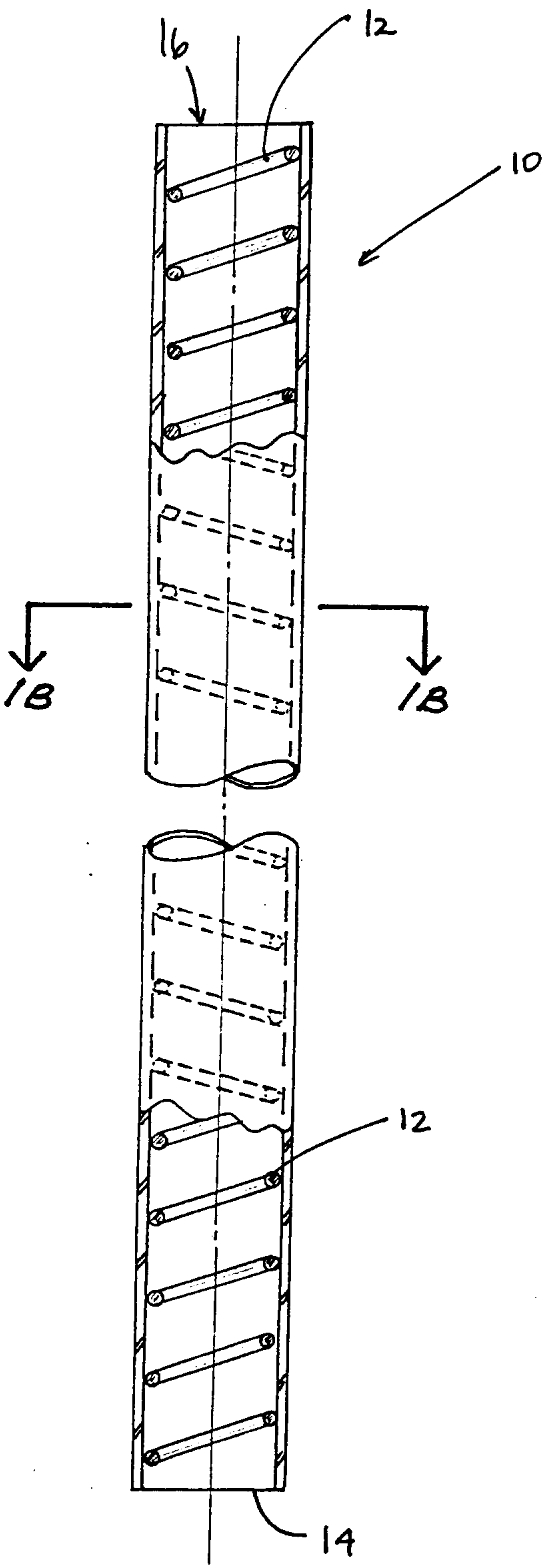


Figure 1a

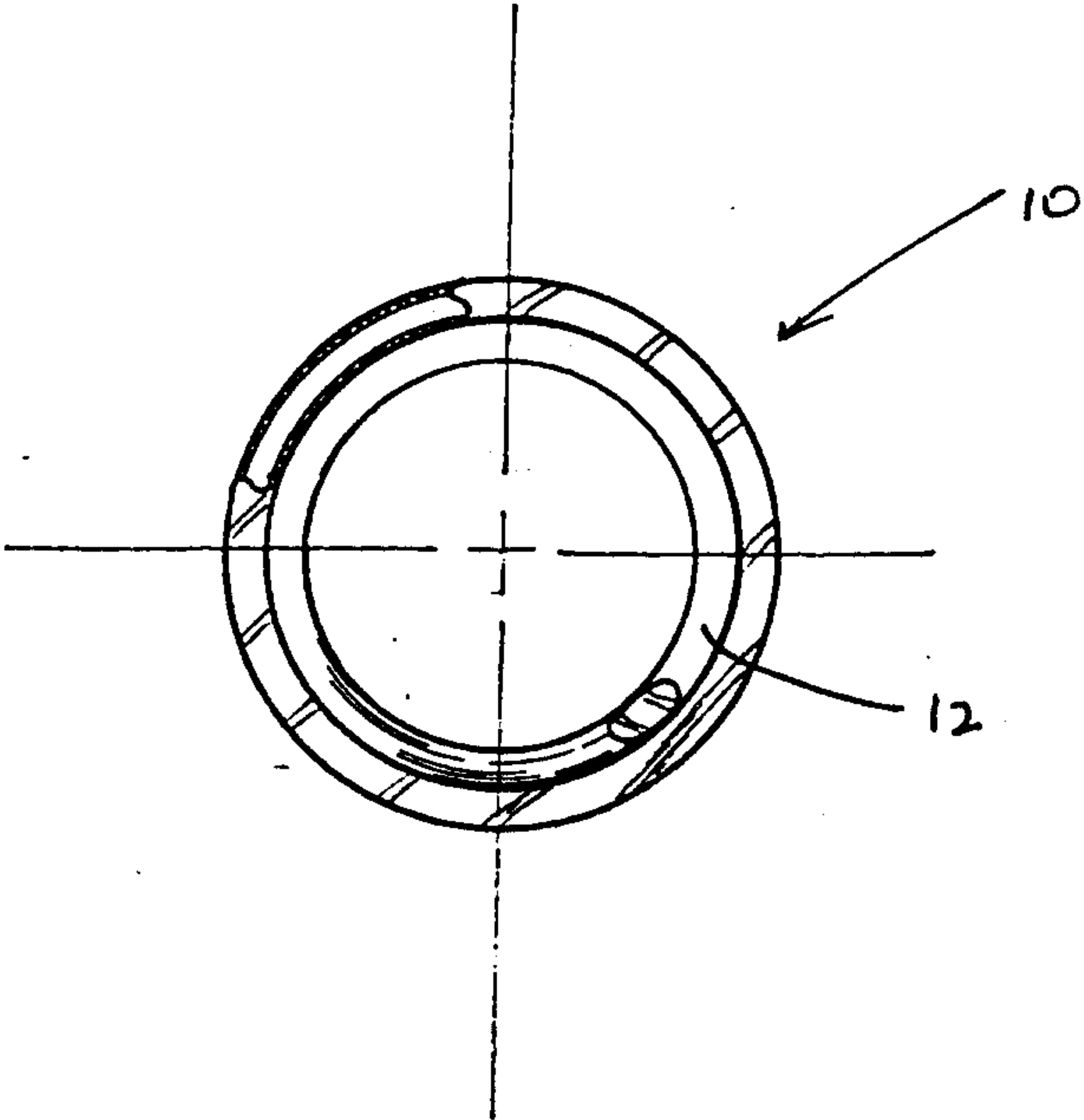


Figure 1b

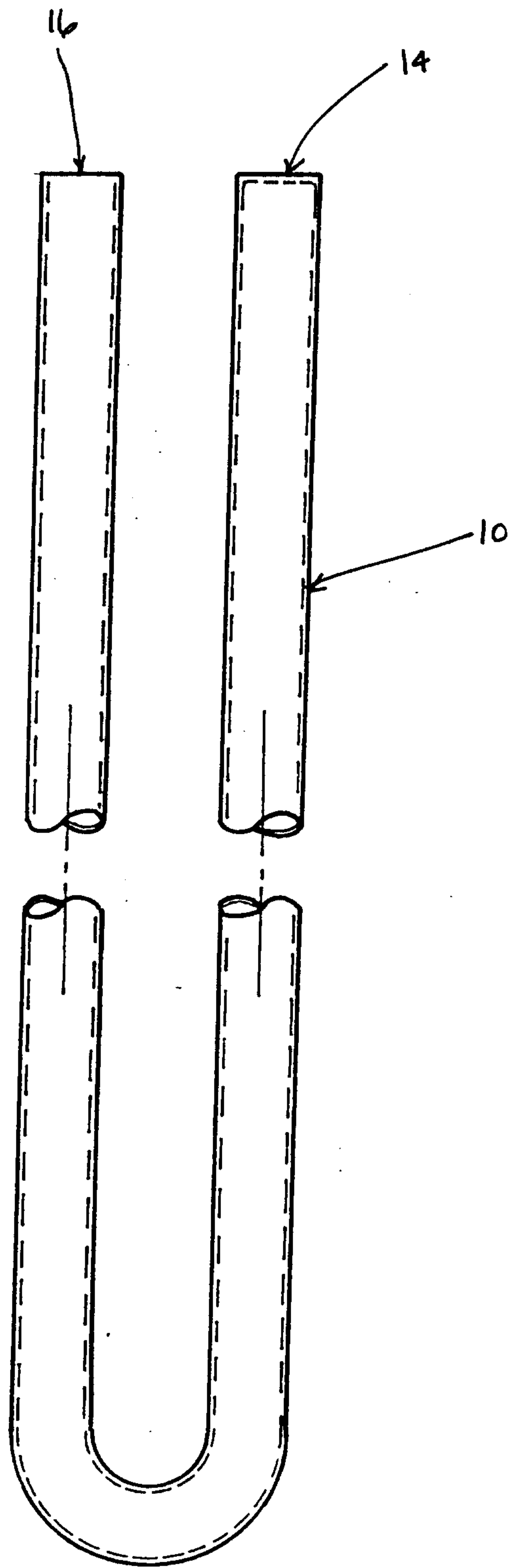


Figure 1c

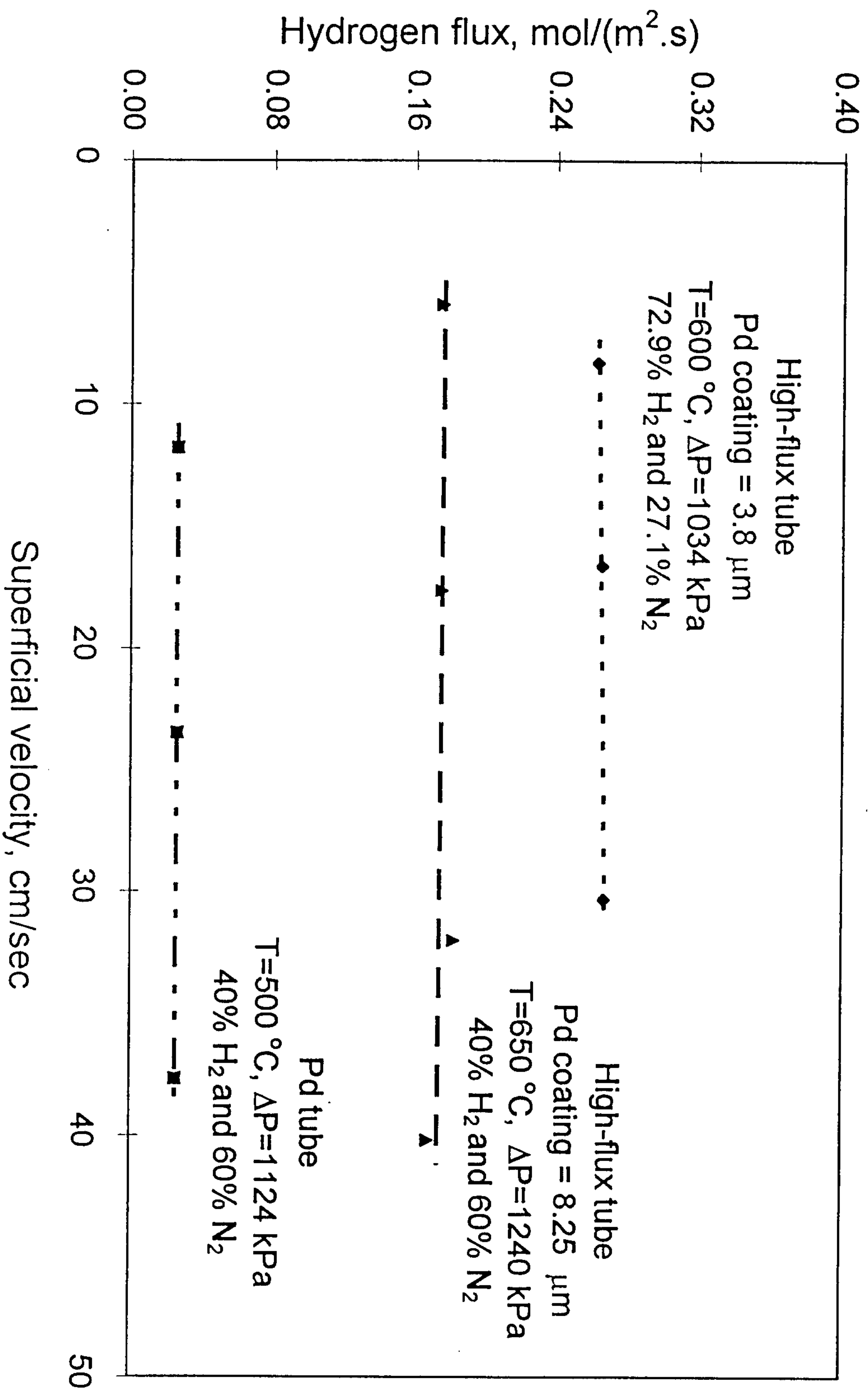


Figure 2

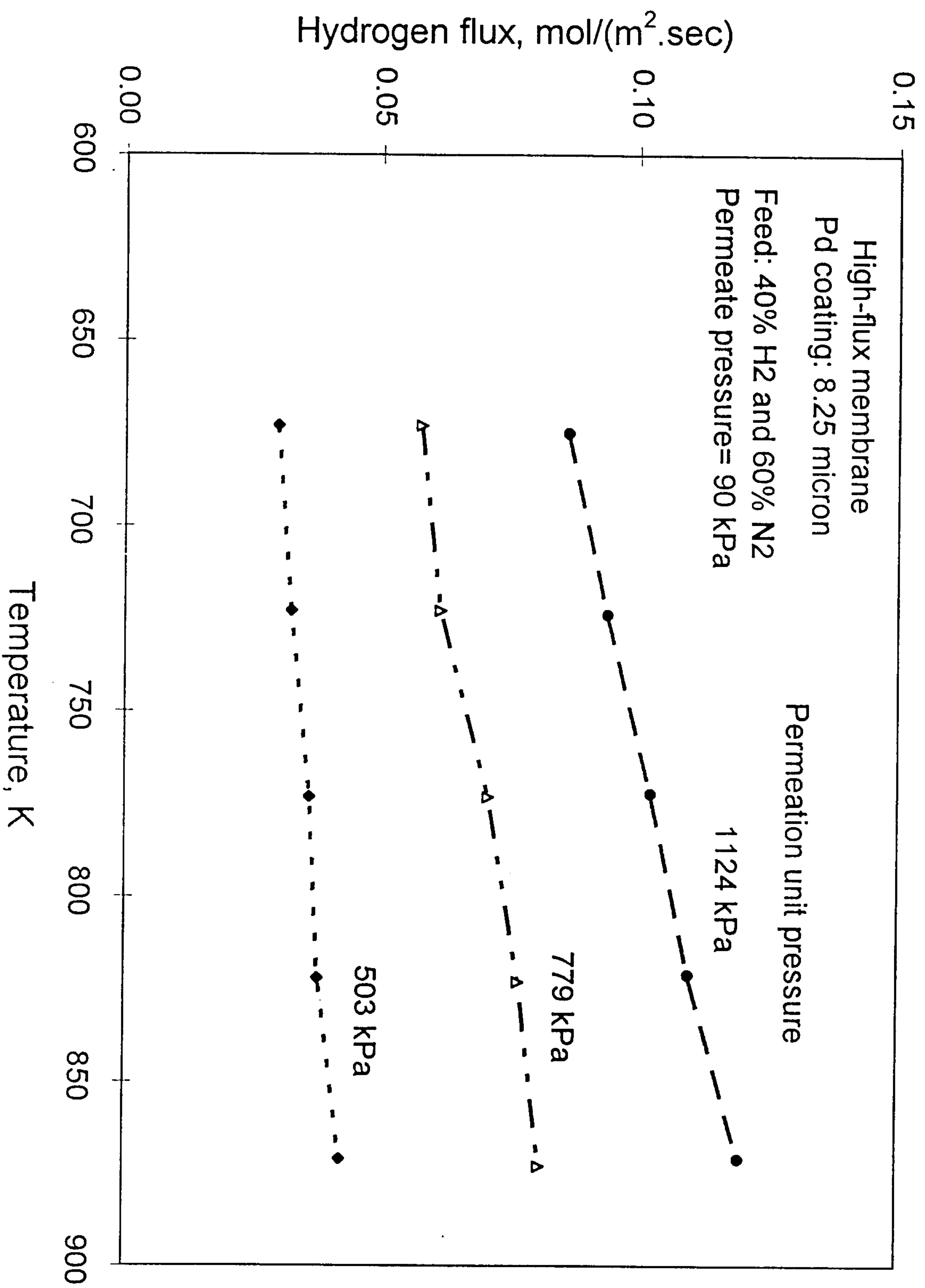


Figure 3

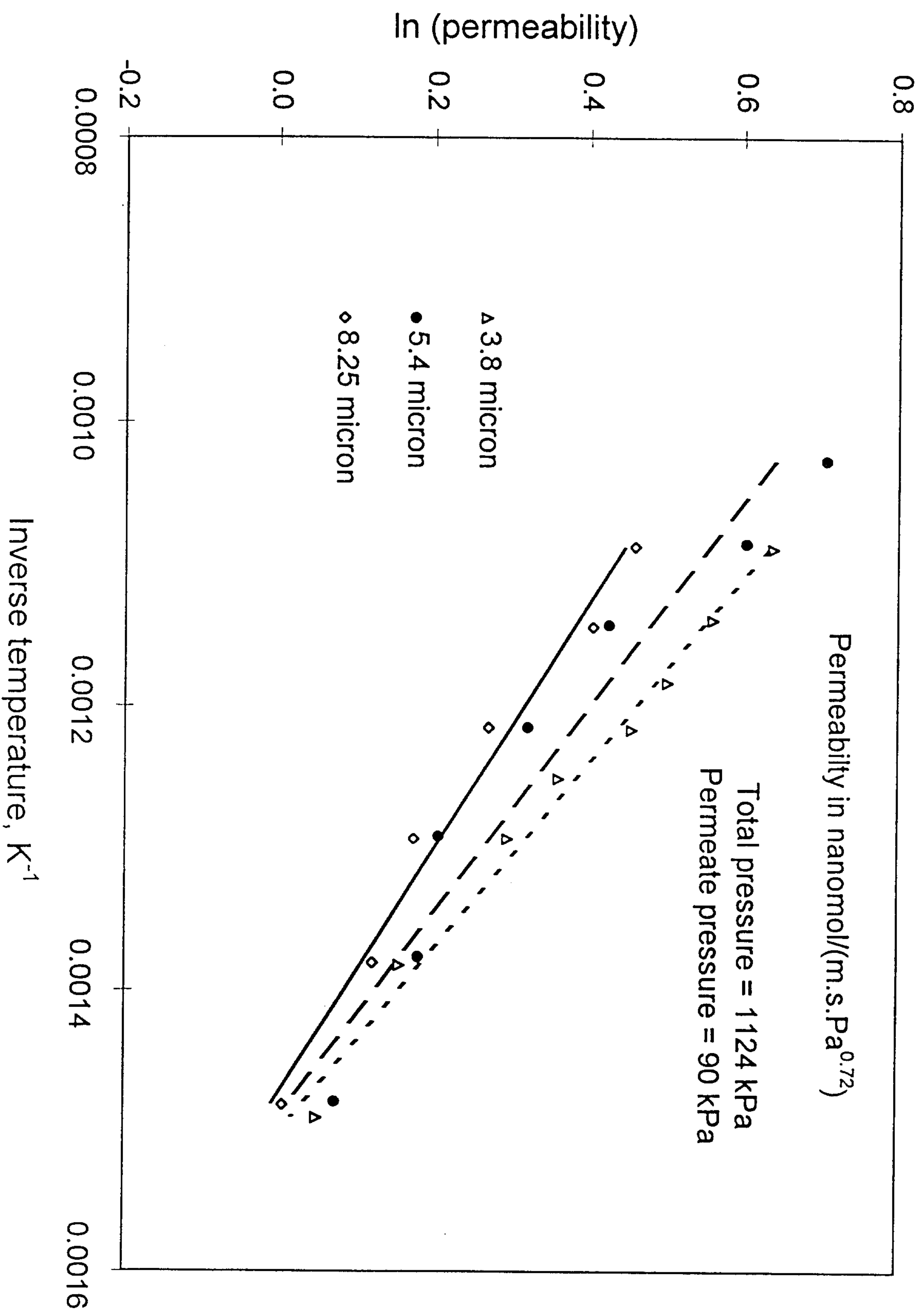


Figure 4

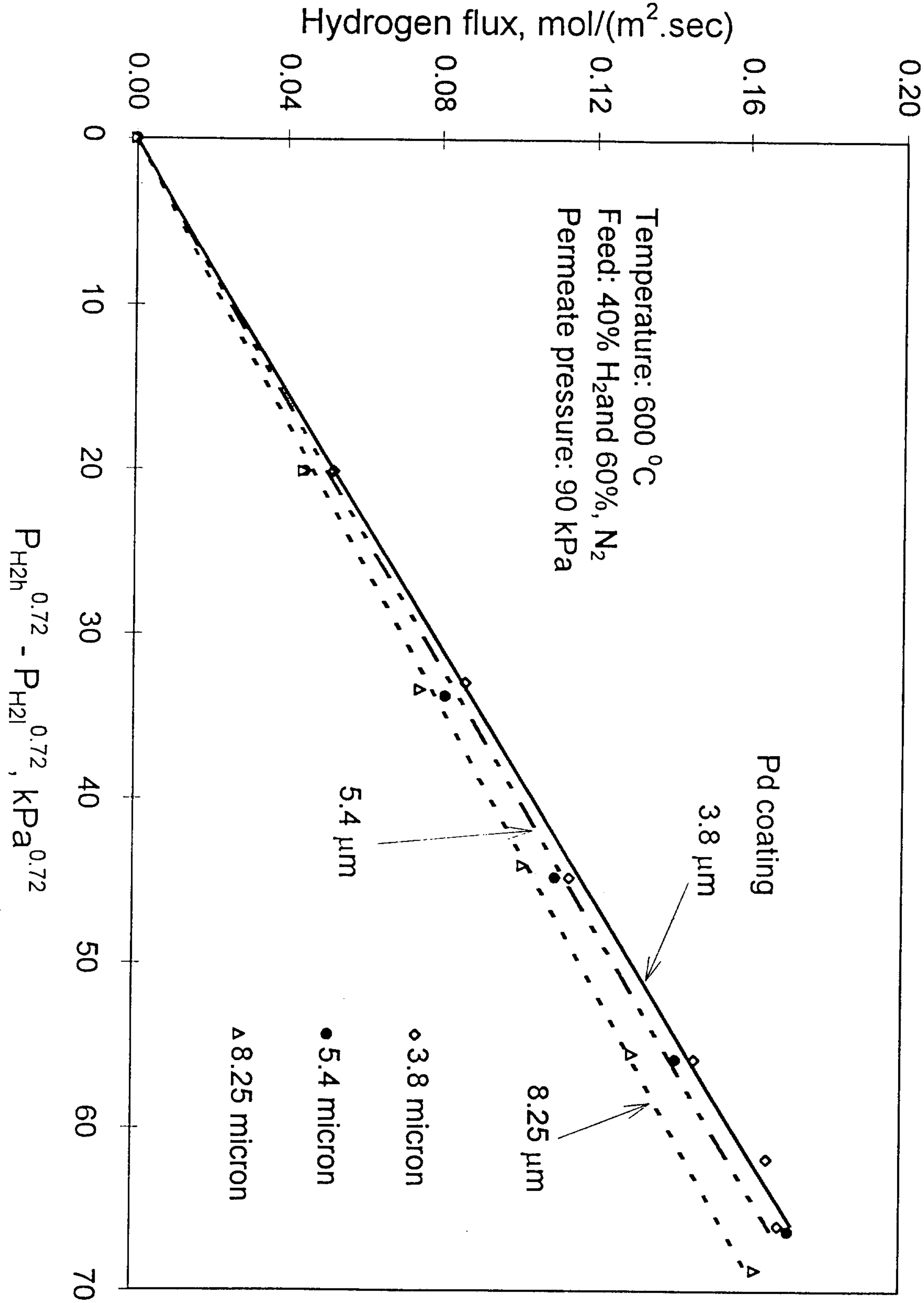


Figure 5

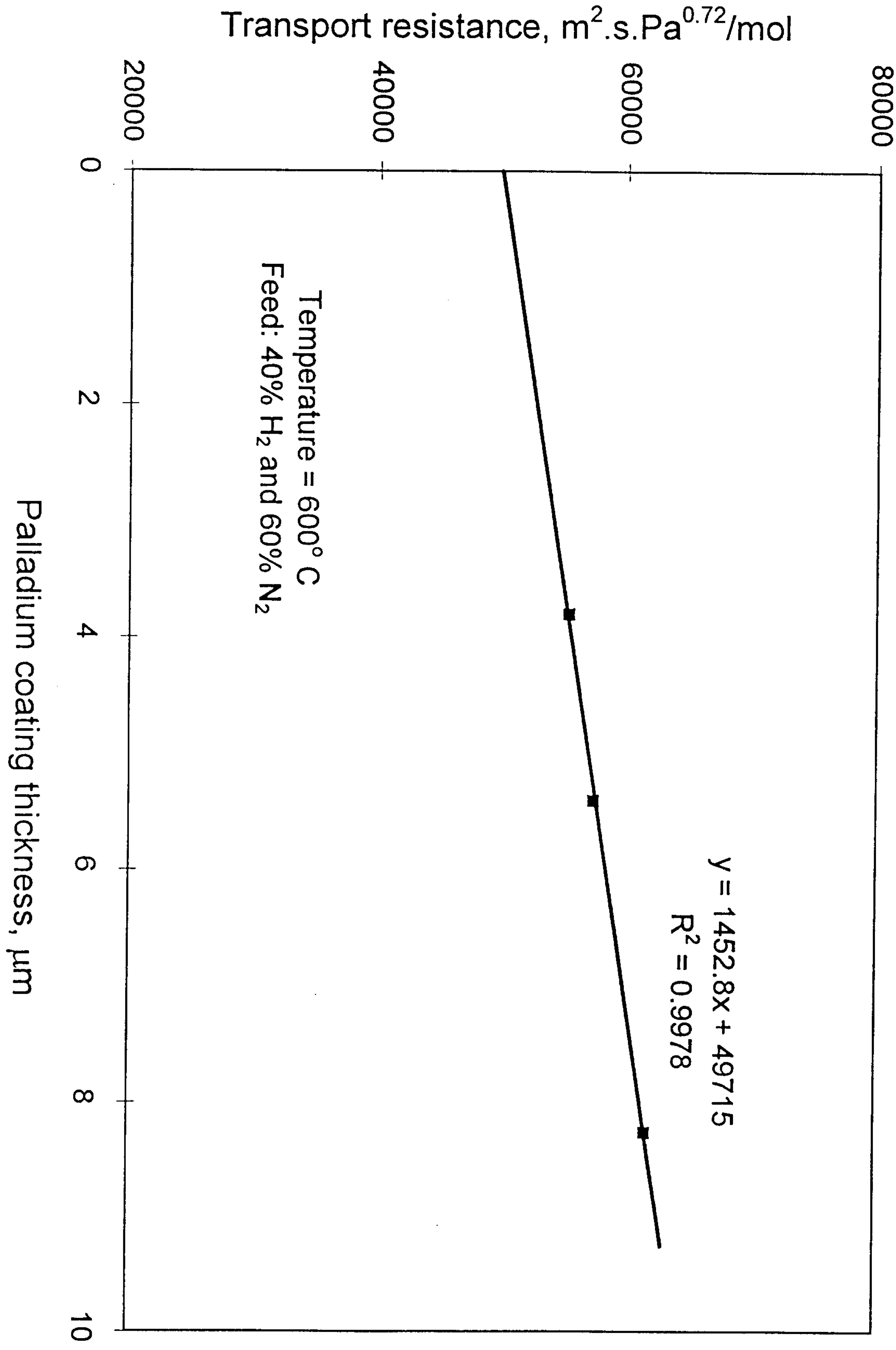


Figure 6

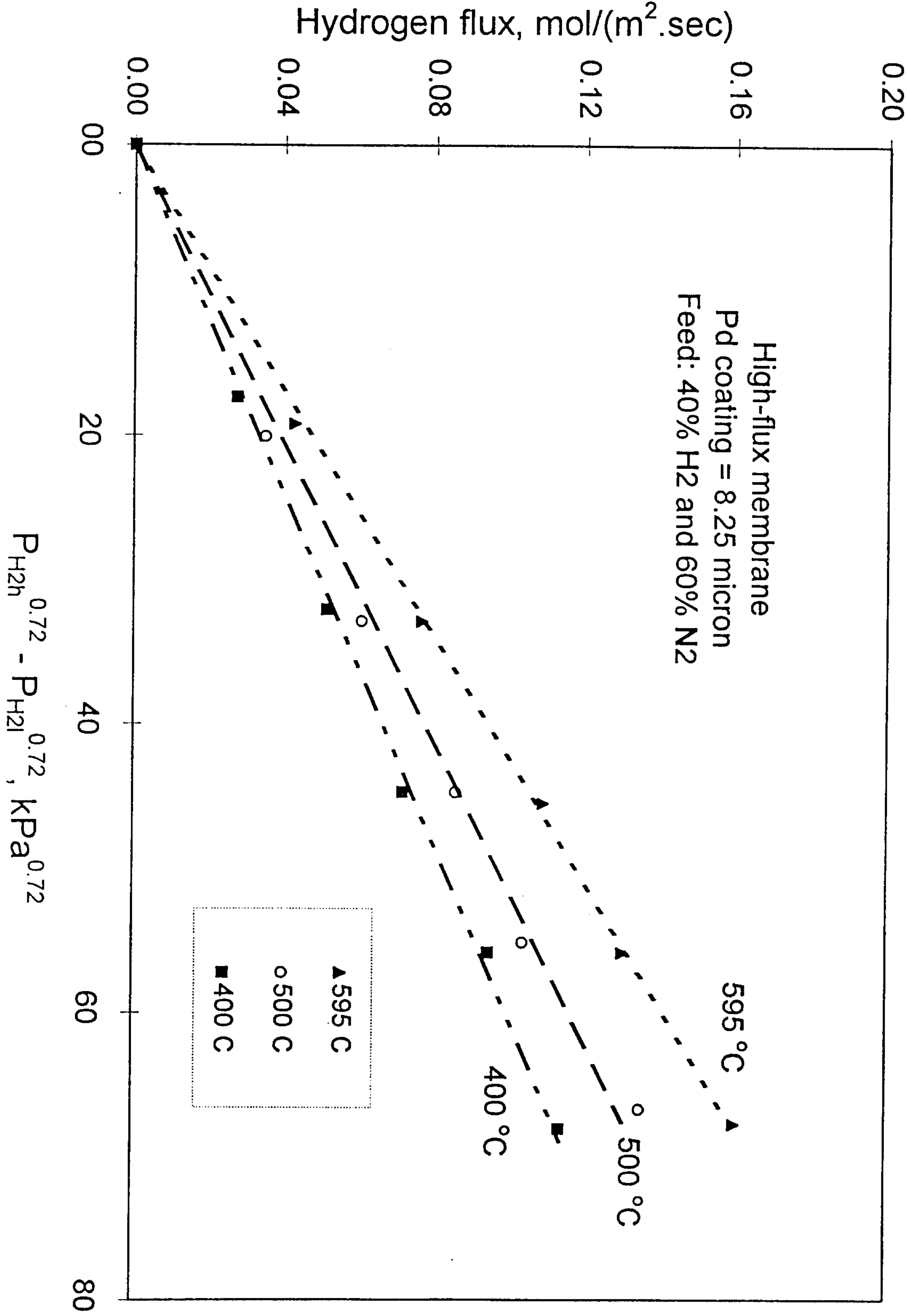


Figure 7

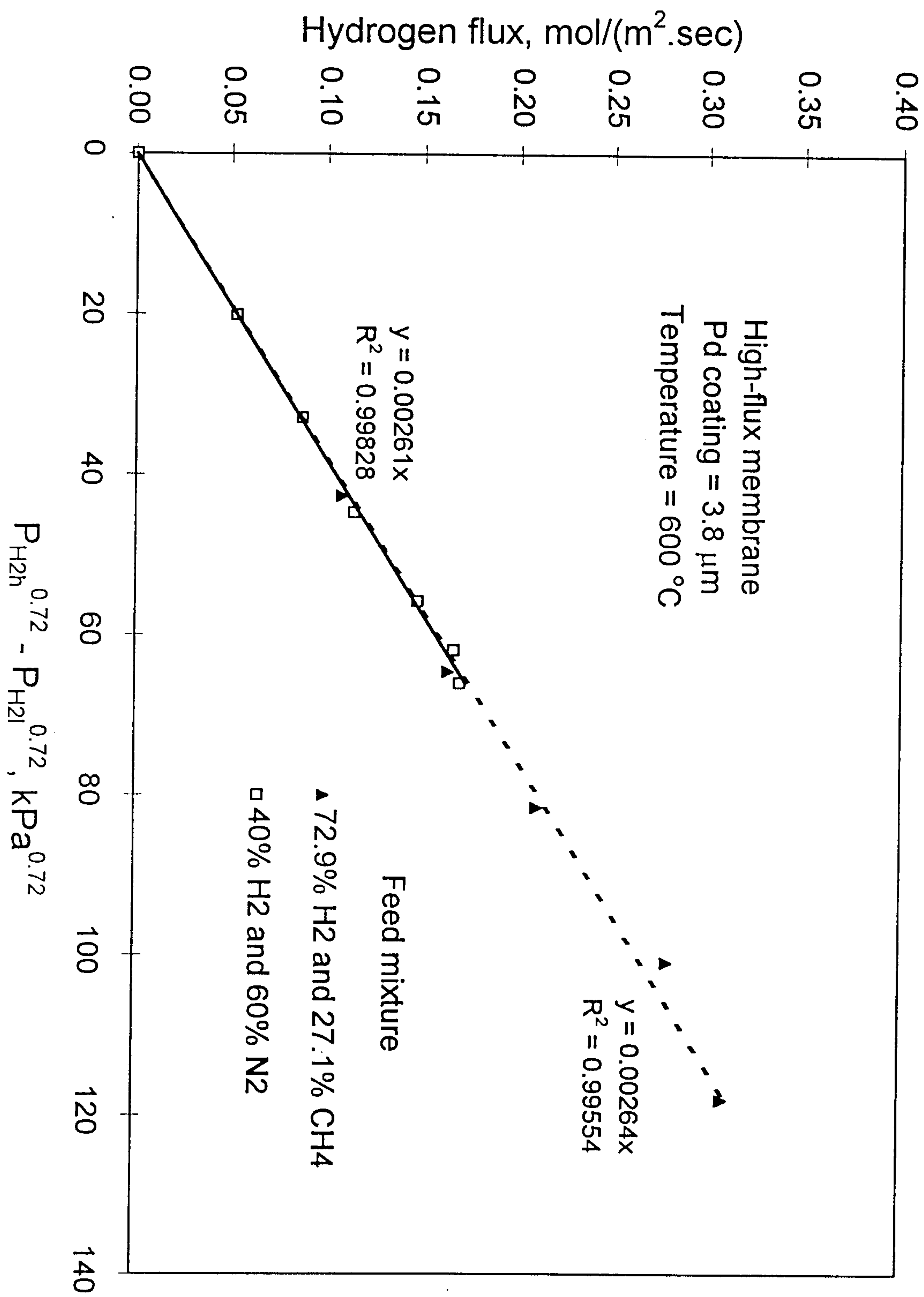


Figure 8

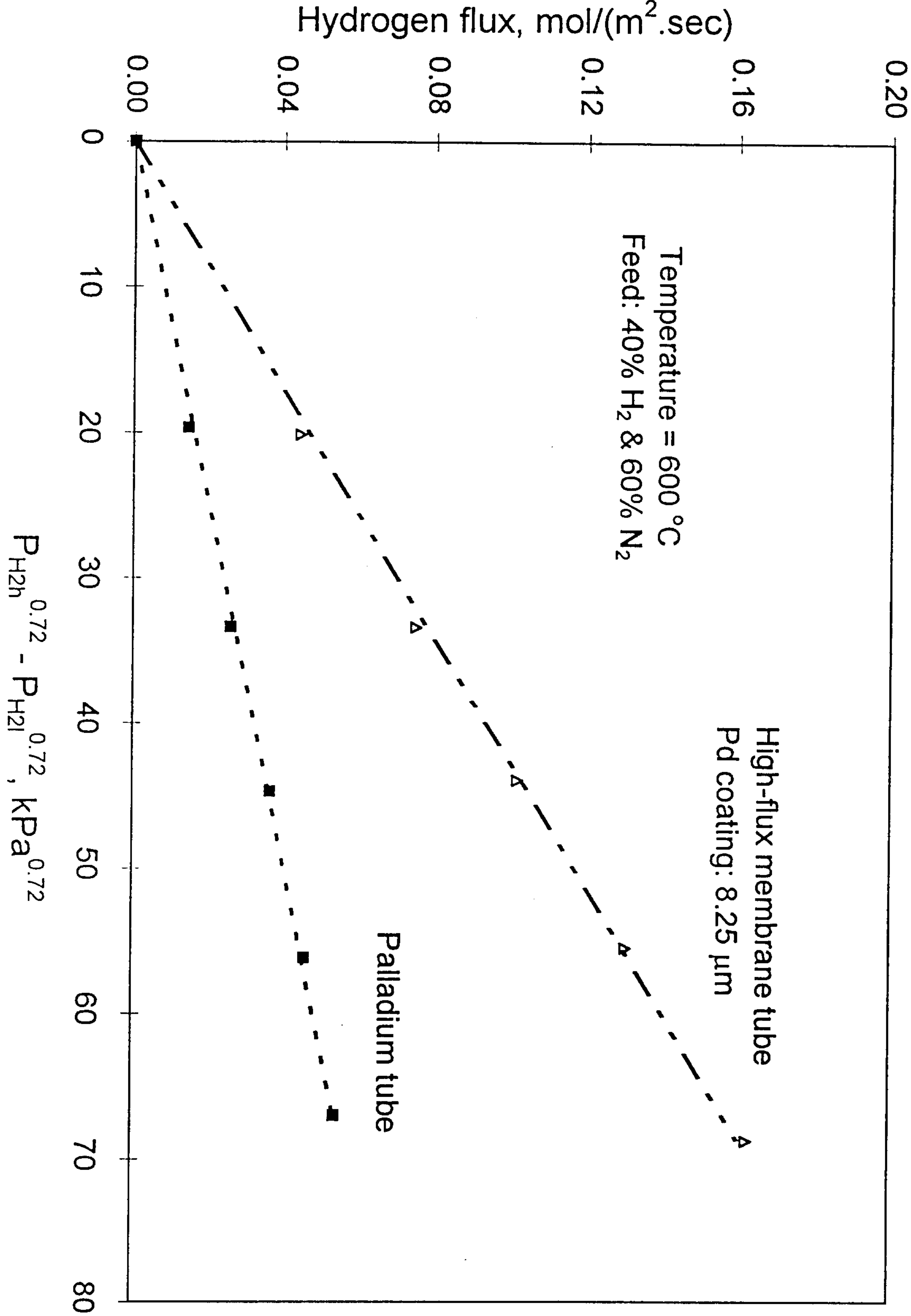


Figure 9

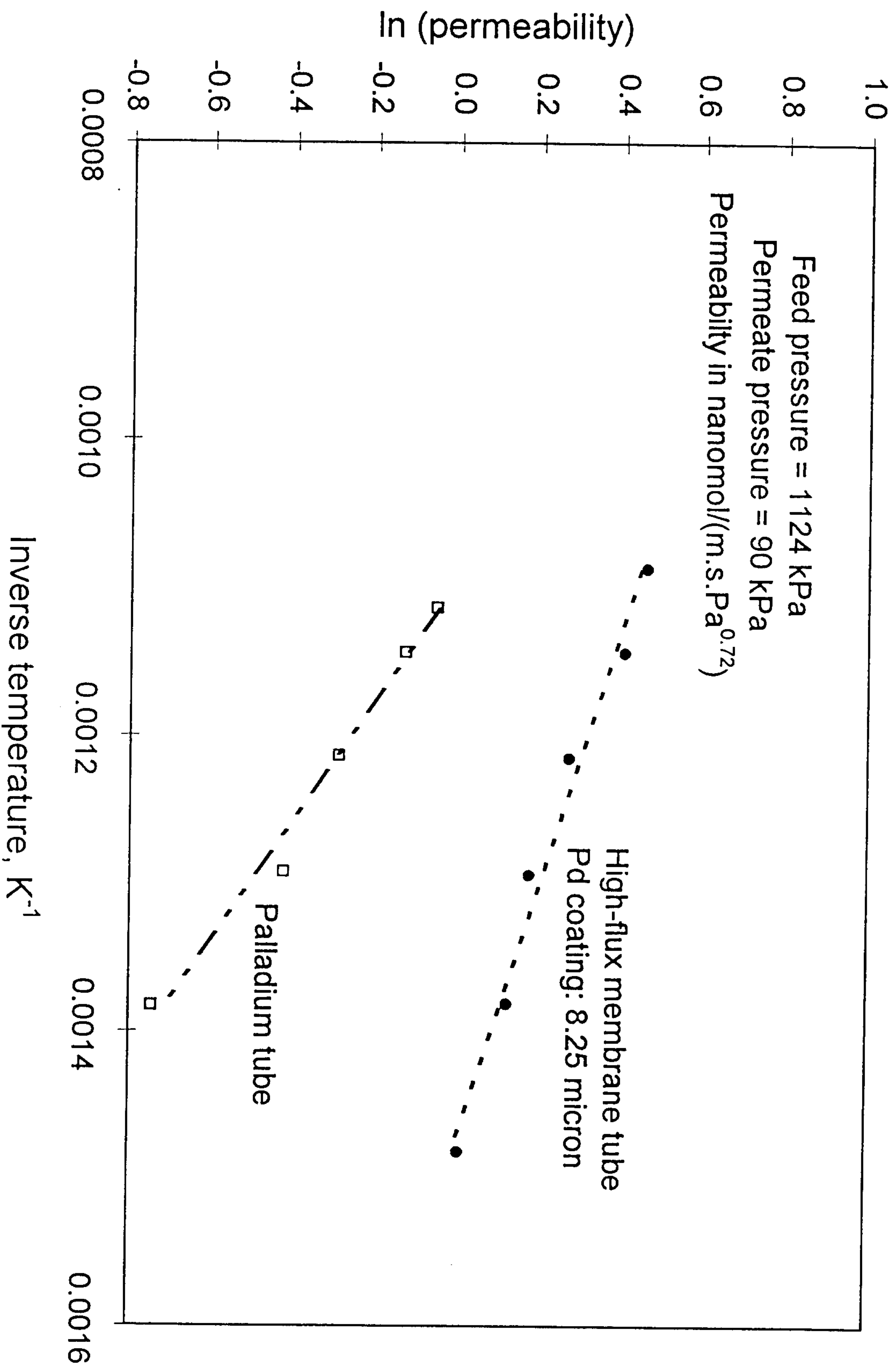


Figure 10