



MEMBRANE BIOREACTORS

Week 2nd: Membranes, Modules, and Cassettes

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CEV4362 MEMBRANE BIOREACTORS

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Time and Room: Wednesday 11:00 - 11:50 FZ-82

12:00 - 12:50 FZ-82

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Week 2nd: Membranes, Modules, and Cassettes

3.1. Membrane Separation Theories

- **Transport of Suspended Particles to the Surface of Membranes and Particle–Membrane Interactions**
- **Transport Theory of Water Molecules through MF and UF Membranes**

3.2. Membrane Materials

3.1. Membrane Separation Theories (1/15)

3.1.1. Transport of Suspended Particles to the Surface of Membranes and Particle–Membrane Interactions

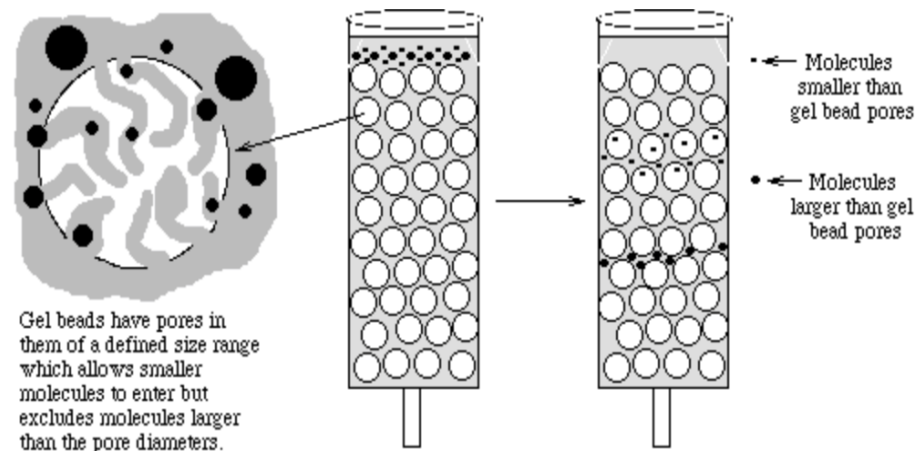
There are two mechanisms by which particles are separated from liquids via filters;

- Depth filtration
- Screen filtration

In **depth filtration**, while the **average pore diameter of a filter is often 10 times bigger than that of the smallest particle that is able to go through the pores**. The main mechanism of depth filtration is **adsorption**. The filter should be regenerated by flushing out adsorbed particles or by substituting it with a new membrane.

Examples of depth filtration;

- ✓ include granulated activated carbon column filters
- ✓ sand filters
- ✓ dual-media filters



3.1. Membrane Separation Theories (2/15)

In screen filtration, the average pore diameter of a filter is smaller than the particles to be removed, which is called a sieving mechanism.

In this mechanism, when particles in the source water (influent water) side are rejected and accumulate on the surface of the membrane. This results in good rejection performance, but high particle accumulation should be taken into account.

Most microfiltration (MF) and ultrafiltration (UF) membranes for MBR processes are screen filters.

When particles in the source water are filtered by membranes, complex transport mechanisms need to be considered;

- a. The transport of suspended particles to the surface of MF and UF membranes.
- b. The transport of water molecules through the membrane pores.

3.1. Membrane Separation Theories (3/15)

a. Transport of Suspended Particles to the Surface of Membranes and Particle–Membrane Interactions

The mechanism of fluid transport in fluid–solid separation is mainly viscous flow in the case of liquid suspensions.

Usually, the flow field inside the membrane is calculated as the result of the action of an externally applied pressure drop across both sides of the membrane where influent flows in and effluent flows out as a driving force for particle separation.

Mechanisms of permeation through or rejection from a membrane depend on;

- The relative size of the suspended particles
- Membrane pores
- on particle–wall interactions

3.1. Membrane Separation Theories (4/15)

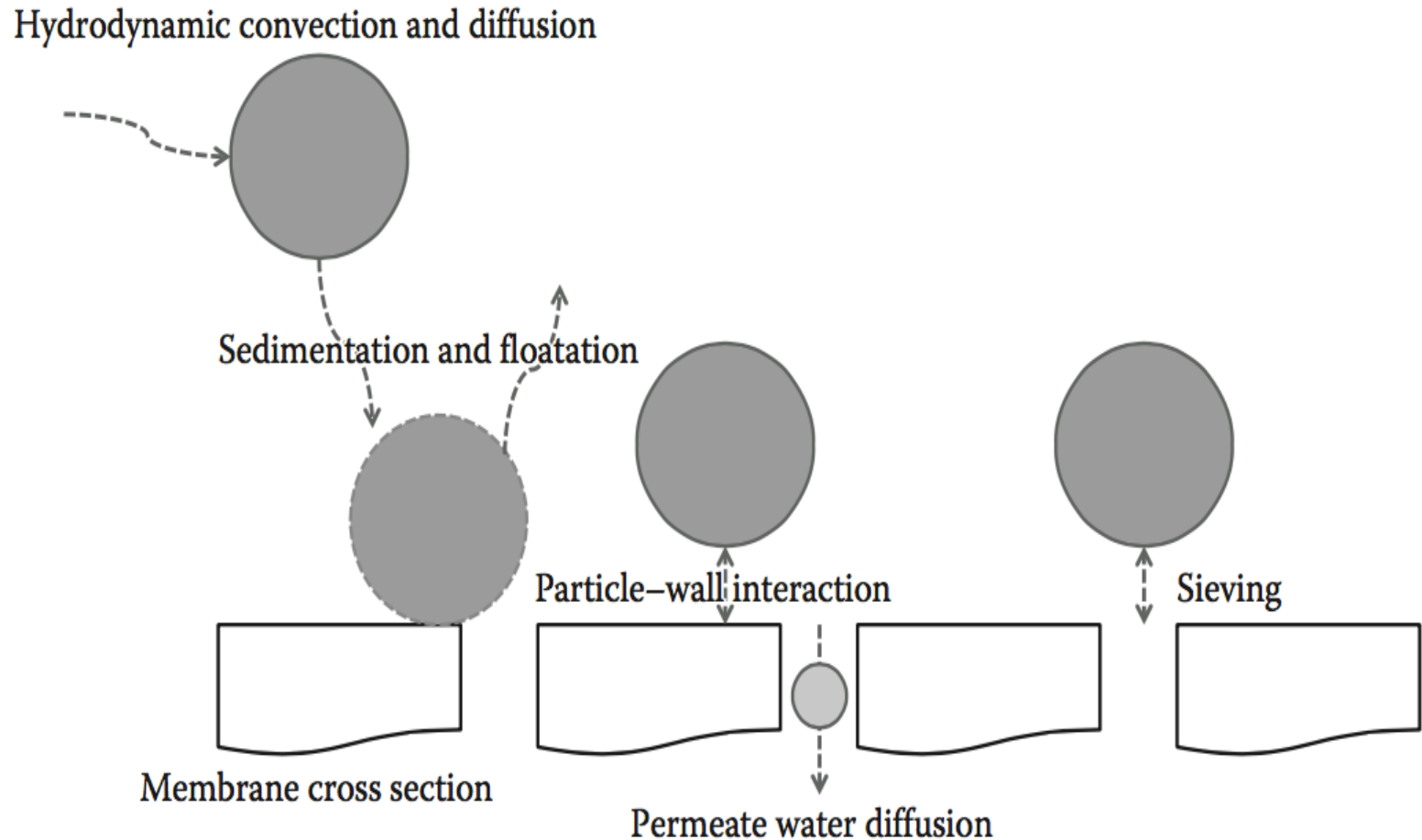


Figure 3.1. Transport mechanism of suspended particles to the surface of membranes.

3.1. Membrane Separation Theories (5/15)

Hydrodynamic Convection:

General particles carrying mechanism is that the hydrodynamic pressure difference **between the inflow and permeate flow or concentrate flow.**

As the particles approach the pore walls, significant hydrodynamic resistance hinders their collision with the solid surface and the resistance increases rapidly with decreasing clearance and tends to infinity upon contact if both the particle and the wall are nonporous. If at least one of the two bodies is permeable, then the hydrodynamic resistance remains finite as the stress that is applied to the fluid is dissipated into the porous body.

Intensive analytical and numerical efforts have been made to calculate correction factors for the classical Stokes hydrodynamic force expression for both porous and nonporous bodies during normal or tangential motion of the particles relative to the pore wall.

3.1. Membrane Separation Theories (6/15)

Sedimentation and Flotation:

Gravitational effects are usually significant for particles larger than about 1 μm (in wastewater treatments, general influent contains particles **larger than 1 μm**). Density of particles effects that of the **carrying fluid, sedimentation or flotation**

In most cases gravitational effects act in combination with other migration mechanisms,

- hydrodynamically driven migration
 - electrokinetic double-layer interaction
 - van der Waals force
- When the distance between particles and membrane wall is very close

3.1. Membrane Separation Theories (7/15)

Particle-Wall Interaction:

In the vicinity of the pore walls, particle–surface interactions become significant, and as the particle approaches the wall, they become dominant. **Waals and electrokinetic double-layer** interactions determine the motion of particles in the close vicinity of the pore walls.

Attraction is caused by the former and, usually, —depending on the sign of surface and solution charges—to a net repulsion at clearances smaller than a critical value due to the switch of the double-layer forces to rapidly increasing repulsive ones.

3.1. Membrane Separation Theories (8/15)

Sieving:

Size exclusion–based separation is theoretically the simplest mechanism of retention of suspended particles that can also lead to very high filtration efficiencies.

However, a small pore size usually implies unacceptably low permeation, which decreases further during filter operation due to the creation of a cake, or a buildup of retained particles, on the feed side of the membrane requiring some special treatment for its removal, typically backwashing.

3.1. Membrane Separation Theories (9/15)

Particle Diffusion:

In liquid filtration, Brownian diffusion may become a significant transport mechanism for submicron particles ($<1 \mu\text{m}$).

For sufficiently small values of “particle diameter/membrane pore diameter” ratio, particles are rejected by membrane pores.

3.1. Membrane Separation Theories (10/15)

Ordinary diffusion coefficient is replaced by the Brownian diffusivity (BD);

$$BD = \frac{C_s k_B T}{3\pi\mu d_{\text{par}}}$$

C_s is the Cunningham correction factor, unitless

k_B is the Boltzmann constant, J/K or (kg m²/s²) K

T is the absolute temperature, K

d_{par} is the effective particle diameter, m

μ is the viscosity of water, kg/m s

3.1. Membrane Separation Theories (11/15)

Example 3.1

Calculate the BD of particles that have 10 μm of diameter flows in water at 20°C in given conditions. Use the information of the Cunningham correction factor C_s at a given temperature in Table 3.1.

Solution

In Table 3.1 two literatures show the Cunningham correction factor of 10.0 μm diameter of particles at a given temperature, which is 1.02, and the viscosity of water at 20°C is $1.002 \times 10^{-3} \text{ kg/m s}$. Therefore the BD of the particles can be calculated using Equation 3.1 as follows:

$$\text{BD} = \frac{C_s k_B T}{3\pi\mu d_{\text{par}}} = \frac{(1.02)(1.38 \times 10^{-23} \text{ (kg m}^2/\text{s}^2) \text{ K})(298 \text{ K})}{(3)(\pi)(1.002 \times 10^{-3} \text{ (kg/m) s})(10^{-5} \text{ m})} = 4.44 \times 10^{-14} \text{ m}^2/\text{s}$$

3.1. Membrane Separation Theories

Table 3.1 Cunningham Correction Factors in Two Literatures

d_p (μm)	Cunningham Correction Factor, C_s	
	<i>Davies (1945)</i>	<i>Allen and Raabe (1982)</i>
0.01	22.7	22.4
0.02	11.6	11.6
0.05	5.06	5.09
0.1	2.91	2.94
0.2	1.89	1.90
0.5	1.34	1.32
1	1.17	1.16
2	1.08	1.08
5	1.03	1.03
10	1.02	1.02
20	1.01	1.01

3.1. Membrane Separation Theories (12/15)

If both hydrodynamic drag and Brownian forces are significant, particle displacement results from the combination of;

- ✓ a **convective step** (determined solely by the local fluid velocity and the time step) and
- ✓ a **Brownian step** (of random direction and with magnitude that is determined by the BD and the time step).

3.1. Membrane Separation Theories (13/15)

3.1.2. Transport Theory of Water Molecules through MF and UF Membranes

The Hagen–Poiseuille equation considers membranes as a number of parallel cylindrical pores perpendicular or oblique to the membrane surface, and there is Laminar flow through a capillary of radius R_p . The water flow per cylindrical pore is given by

$$Q_c = \frac{\pi R_p^4}{8\mu} \times \frac{\Delta P}{\Delta x}$$

μ is the viscosity of water, Pa s

ΔP is the pressure difference, Pa

Δx is the membrane thickness, μm

R_p is the pore diameter, μm

3.1. Membrane Separation Theories (14/15)

If the membrane has N number of capillary pores, then the total flow through the membrane (Q_p or Q_w) is

$$Q_p \quad \text{or} \quad Q_w = NQ_c$$

And effective membrane pore area (A) is calculated as follows:

$$A = \frac{N\pi R_p^2}{\epsilon}$$

N is the number of pores

ϵ is the porosity of membrane, unitless

The permeate flux through a membrane is the permeate flow divided by the effective area of flow surface and is given by

$$J_w = \frac{NQ_c}{A} = \frac{NQ_c}{(N\pi R_p^2/\epsilon)} = \frac{N\left(\left(\pi R_p^4/8\mu\right) \times (\Delta P/\Delta x)\right)}{(N\pi R_p^2/\epsilon)} = \frac{\epsilon R_p^2}{8\mu} \times \frac{\Delta P}{\Delta x}$$

3.1. Membrane Separation Theories

Example 3.2

Assume that the pore shape of a membrane is cylindrical and the membrane has only one pore with a length of 1 mm. Once the inner pore is wet enough and the hydraulic pressure is applied between the two ends of the pore, then water flows from the source water side to the permeate side with a linear velocity of 100 cm/s. Assume that the hydraulic pressure is 0.2 bar and the temperature is a constant 20°C. Calculate the inner diameter of the membrane pore.

Solution

Because the pore shape of the membrane is cylindrical, we can use the Hagen–Poiseuille equation to get the inner diameter of the membrane pore. We have to first calculate the flow rate per cylindrical pore by multiplying the linear velocity of the cross-sectional area:

$$Q_c = v \times \pi R_p^2 = \frac{\pi R_p^4}{8\mu} \times \frac{\Delta P}{\Delta x}$$

$$v = \frac{R_p^2}{8\mu} \times \frac{\Delta P}{\Delta x}$$

$$R_p = \sqrt{8\mu v \times \frac{\Delta x}{\Delta P}}$$

$$R_p = \sqrt{((8)(1.002 \times 10^{-3} \text{ Pa s})(10^3 \mu\text{m} \times 10^6 \mu\text{m/s})/((\pi)(0.2 \times 10^5 \text{ Pa}))} = 11.3 \mu\text{m}$$

Therefore the inner diameter of the membrane pore is 11.3 μm.

3.1. Membrane Separation Theories (15/15)

In reality, pores are not straight, so the previous equation should include a factor for the tortuosity of pores (τ) and $\epsilon R_p^2 / 8\mu\tau$. This factor is abbreviated as K_p and is called hydraulic permeability:

$$J_w = \frac{\epsilon R_p^2}{8\mu\tau} \times \frac{\Delta P}{\Delta x} = K_p \times \frac{\Delta P}{\Delta x}$$

Meanwhile Kozeny and Carman (1939) assumed that membranes are a system of closely packed spheres and derived permeate flux as follows:

$$J_w = \frac{\epsilon^3}{(1 - \epsilon^2)\mu K S^2} \times \frac{\Delta P}{\Delta x}$$

where

ϵ is the porosity of the membrane, unitless

S is the internal surface area, m^2

K is the Kozeny–Carman constant depending on the shape of pores and tortuosity, unitless

3.2. Membrane Materials(1/5)

Over 130 materials (scientific and patent) have been used to manufacture membranes. Only a few of these membranes have been commercialized, because of the several limitation in water and wastewater treatment like;

- high acidic, basic, chemical, mechanical durability for more than 5 years of operation.
- Resistance of unknown toxic chemicals (including oxidants)

Therefore, robust materials such as engineering plastics, stainless steel, and ceramic materials are preferred by users.

3.2. Membrane Materials(2/5)

Polymer-based membranes are dominated in water and wastewater treatment membrane market. The polymer-based membranes are given below;

- ❖ PSF, Polysulfone
- ❖ PES, Polyethersulfone
- ❖ Polyolefins: PE (polyethylene), PP (polypropylene), PVC (polyvinylchloride)
- ❖ PVDF, Polyvinylidene Difluoride
- ❖ PTFE, Polytetrafluoroethylene
- ❖ CA, Cellulose Acetate

3.2. Membrane Materials(3/5)

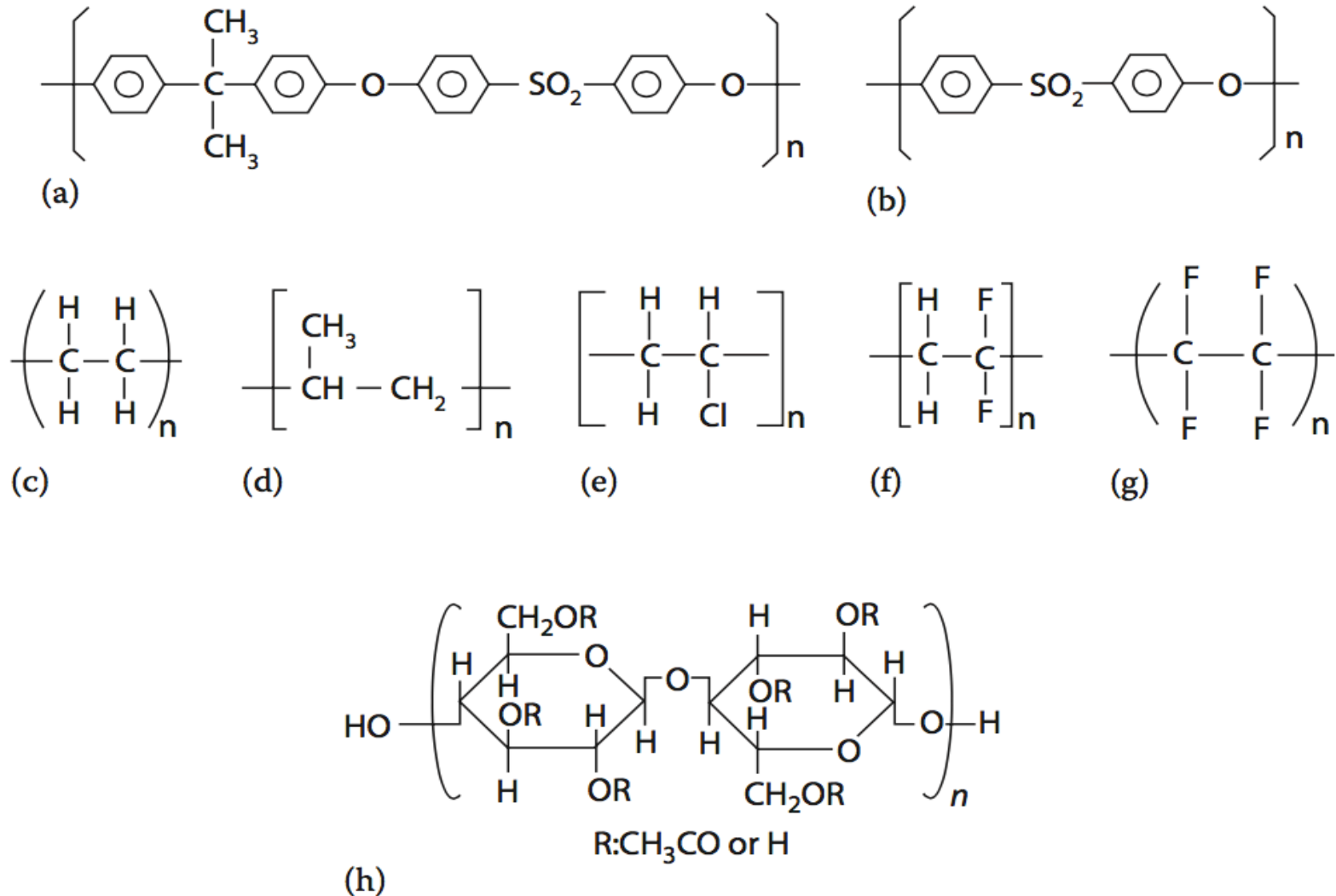


Figure 3.2. Molecular structure of the most commonly used polymers for membranes: (a) PSF, (b) PES, (c) PE, (d) PP, (e) PVC, (f) PVDF, (g) PTFE, and (h) CA.

3.2. Membrane Materials(4/5)

Table 3.1. Membrane Materials

Polymer	Fabrication	Advantage	Disadvantage
PSF	NIPS	<ul style="list-style-type: none"> • Easy to form structure • Safe from leaching • High mechanical strength 	<ul style="list-style-type: none"> • Rigid/brittle • Low chemical durability
PES	NIPS	<ul style="list-style-type: none"> • Easy to form structure • Safe from leaching • High mechanical strength 	<ul style="list-style-type: none"> • Rigid/brittle • Low chemical durability
PE	MSCS	• Low material cost • High elongation	• Wide pore size distribution
PP	MSCS	• Low material cost • High elongation	• Wide pore size distribution
PVC	MSCS	• Low material cost • High elongation	<ul style="list-style-type: none"> • Wide pore size distribution • Side effect by additives

3.2. Membrane Materials(5/5)

Table 3.1. Membrane Materials (Cont.)

Polymer	Fabrication	Advantage	Disadvantage
PVDF	NIPS, TIPS	<ul style="list-style-type: none"> • Narrow pore size distribution • High chemical durability 	<ul style="list-style-type: none"> • Not easy to form structure • Weak to basic condition
PTFE	MSCS	<ul style="list-style-type: none"> • High water permeability • Highest chemical durability • Low fouling potential 	<ul style="list-style-type: none"> • Difficult module fabrication • High material cost
CA	NIPS	<ul style="list-style-type: none"> • Hydrophilic (easily wet) • Easy to form structure 	<ul style="list-style-type: none"> • Low acid/base durability • Low chemical durability

*Non-solvent-induced phase separation (NIPS)

**Thermal-induced phase separation (TIPS)

***Melt spinning cold stretching (MSCS)



Thank you...