

# Polyvinylidene Fluoride using Non-Fluorinated Surfactant

PEP Review 2024-15

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## Glossary

Å	Armstrong
AFPO	Ammonium perfluorooctanoate
AIBN	Azobisisobutyronitrile
APFO	Ammonium perfluorooctanoate
atm	Atmospheres
barg	Bar-gauge
BCM	Billion cubic meters
BFD	Block Flow Diagram
BFW	Boiler feed water
bhp	Brake horsepower
BLI	Battery limits investment
Btu	British thermal units
°C	Degree Celsius
CAGR	Compound annual growth rate
Capex	Capital expenditure
¢/lb	Cents per pounds
CMC	Critical micelle concentration
cP	Centipoise
CTA	Chain transfer agent
CTFE	Chlorotrifluoroethylene
dia	Diameter
DSC	Differential scanning calorimetry
EPA	Environment Protection Agency
°F	Degree Fahrenheit
FDA	Food and Drug Administration
FEP	Fluorinated ethylene-propylene
FKM	Fluorine kautschuk material
FOB	Free on board
ft <sup>3</sup>	Cubic feet
g	Gram
G&A	General and administrative
g/cm <sup>3</sup>	Grams per cubic centimeter
g/ml	Grams per milliliter
g/mol	Grams per mole
gal	Gallon
GHG	Greenhouse gases
gpm	Gallons per minute
GWP	Global warming potential
h	Hour
HDPE	High-density polyethylene
HFC	Hydrofluorocarbons
HFP	Hexafluoropropylene
hp	Horsepower
HVAC	Heating, ventilation and air conditioning
kg	Kilogram
kg/h	Kilograms per hour
kg/m <sup>3</sup>	Kilograms per cubic meter
kHz	Kilohertz
kJ	Kilojoules
kP	Kilopoise
kPa	Kilopascals
kWh	Kilowatt hour
lb	Pound
lb/y	Pounds per year
LCOE	Levelized cost of electricity
m	Meters
M	Thousand
µm	Micrometers
MD	Membrane distillation
Mgal	Thousand gallons

Mlb	Thousand pounds
Mlb/h	Thousand pounds per hour
mm	Millimeters
MMBtu/h	Million British thermal units per hour
MMlb/y	Million pounds per year
MMt	Million metric tons
mol%	Molar percent
MPa	Megapascals
Mscfh	Thousand standard cubic feet per hours
Mt	Metric tons
Nm	Nanometers
NMP	N-Methyl-2-pyrrolidone
Opex	Operating expenditure
PAA	Polyacrylic acid
PCTFE	Polychlorotrifluoroethylene
PDD	Perfluoro (2,2-dimethyl-1,3-dioxole)
PE	Polyethylene
PEP	Process Economics Program
PEG	Polyethylene glycol
PEVE	perfluoro (ethyl vinyl) ether
PFD	Process flow diagram
PFOA	Perfluorooctanoic acid
PHFP	Polyhexafluoropropylene
PMVE	Perfluoro methyl vinyl ether
ppb	Parts per billion
ppm	Parts per million
PPS	Potassium persulfate
PPVE	Perfluoro (propyl vinyl) ether
psi	Pounds per square inch
psia	Pounds per square inch absolute
psig	Pounds per square inch gauge
PTFE	Polytetrafluoroethylene
PTrFE	Polytrifluoroethylene
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
PVF	Polyvinyl fluoride
PZ	piperazine
R&D	Research and development
ROI	Return on investment
s	Second(s)
SAC	Sodium acetate
scf	Standard cubic feet
SCGT	Simple Cycle Gas Turbine
SCM	Standard cubic meter
sq ft	square feet
SDS	Sodium dodecyl sulfate
SS	Stainless steel
TFC	Total fixed capital
TFE	Tetrafluoro ethylene
ton-h	Refrigeration ton-hour
TrFE	Trifluoroethylene
t/t	Metric tons per metric ton
t/y	Metric tons per year
USGC	United States Gulf Coast
UV	Ultraviolet
VDF	Vinylidene fluoride
VOC	Volatile organic compounds
vol%	Volume percent
w/w	Weight for weight
wt%	Weight percent

# Abstract

Polyvinylidene fluoride (PVDF) is one of the most widely used fluoropolymers available today. It is frequently employed as membrane and binder materials, and in pipes and cables. PVDF is now being investigated for its use in wastewater management, chemical engineering, biomedical research, and batteries. Because of its exceptional physicochemical qualities, PVDF is used in a majority of developing technologies. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) is a copolymer formed by the emulsion polymerization of vinylidene fluoride (VDF) with hexafluoropropylene (HFP). The insertion of the HFP group in VDF polymer improves its characteristics since the fluorine segment is hydrophobic and has a low polarity. PVDF-HFP has higher solubility (particularly in organic solvents), hydrophobicity, mechanical strength, a lower glass transition temperature, reduced crystallinity, and a higher free volume than PVDF.

This study covers the semibatch emulsion polymerization process of PVDF-HFP copolymer, which is obtained from VDF with comonomer HFP, in an aqueous medium containing a non-fluorinated surfactant. Usually, an aqueous medium is used in a semibatch emulsion or suspension polymerization process to convert VDF into PVDF. A free-radical initiator, a fluorinated surfactant (such as ammonium perfluoro decanoate), and a chain transfer agent (CTA) are used in the polymerization operations. Fluorinated surfactants are stabilized compounds that are often costly and have a high degree of environmental persistence due to their high stability. Fluoroalkyl surfactants are resistant to chemical breakdown, and therefore, may build up in the environment and in living things. Additionally, the surfactant's high degree of fluorination prevents atoms from transferring from the surfactant to a developing polymer chain during polymerization, which will likely inhibit the reaction and lower the product's molecular weight.

This review addresses the technical and financial aspects of producing commercial-grade PVDF-HFP copolymer with a capacity of 22.05 MMlb/y (10,000 t/y) using the emulsion copolymerization of VDF with HFP (7.2 wt%). The process flow diagram, material balance, major equipment list with specifications, cost information for battery limits and offsites, variable costs, capital expenditure (capex) and operating expenditure (opex), the levelized cost of electricity (LCOE), and total production cost are included in this assessment. Process Economics Program (PEP)'s independent interpretation of the commercial process, based on data from publicly available sources, including technical articles and patents, is the basis for the economic evaluation provided in this review. It may not accurately depict the actual plant layout, either whole or in part.

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