MULTIWAY PARTIAL LEAST SQUARE FOR MODELING AND MONITORING OF POLY METHYL METHACRYLATE REACTOR

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by

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LIST OF ABBREVIATIONS

AIBN	2, 2’-azobisisobutyronitrile
BPO	Benzoyl Peroxide
CF	Coolant flowrate
CSTR	Continuous stirred tank reactor
E	X residual
F	Y residual
FPM	First Principle Model
GLC	Globally linearizing control
GPC	Generalized predictive control
I	Batches
J	Input variables
JT	Jacket temperature
K	Times in MPLS model
LDPE	Low-density polyethylene
M	Output variables
MC	Monomer conversion
MLR	Multiple linear regressions
MMA	Methyl Methacrylate
MPLS	Multiway Partial Least Squares
MSE	Mean square error of prediction
Mw	The weight average molecular weight
Mn	The number average molecular weight
N	Number of measurement

NIPALS	Nonlinear iterated partial least square
NLPCA	Nonlinear Partial Least Squares
P	Loading X
PID	Proportional Integral Derivative
PC	Principal Component
PCA	Principal Component Analysis
PLS	Partial Least Squares
PVC	Polyvinyl chloride
Q	Loading Y
RMSE	Root Mean Squared error
RT	Reactor temperature
SBR	Styrene-butadiene rubber
Std	Standard deviation
T	Score X
U	Score Y
X	Input data
X_{mean}	Mean of X data
X_{std}	Standard deviation of X data
Y	Output data
Y_{mean}	Mean of Y data
Y_{std}	Standard deviation of Y data

LIST OF SYMBOLS

Symbol	Description	Unit
A (T)	Temperature dependant parameter in gel effect model	-
At	Heat transfer area	m^2
B	Constant parameter in gel effect model	-
C_p, C_{pc}	Specific heats for mixture and coolant, respectively	kJ/ (kg K)
D	Intermediate variable in the gel and glass effect models	-
f	Intermediate variable in the gel and glass effect models	-
I, I_0	Initiator and initial initiator concentration, respectively	mol / l
k_d	Dissociation rate	L/min
k_{po}, k_{t0}	Overall propagation and termination rate constants at zero monomer conversion	L/min-mol
k_{td} ,k_{tc}	Termination by combination and disproportiation reaction rate constant	L/min
M_c	Coolant flow rate	g/min
M, M_0	Monomer and initial monomer concentration	mol/l
q	Heat from the electrical heater	W
R_h	The overall heat transfer coefficient	J
R_m	Rate of monomer consumption	mol/L
t	Time	min

T	Temperature	K
T_c, T_{ci}, T_{co}	Average, inlet and outlet coolant temperature, respectively	K
T_{gp}	Glass transition temperature	K
U	Overall heat transfer coefficient	W/ (m^2 K)
V, V_c	Reactor and coolant volume, respectively	m^3
x	Monomer histories for the reaction at 70^{0}C.	-

Greek letters

θ_p	temperature-dependant parameter in gel effect model
θ_t	temperature and initiator loading concentration dependant parameter in gel effect model
ρ , ρ_c	density of mixture and coolant, respectively
τ_d, τ_i	derivative and integral time constant
$-\Delta H_p$	heat of polymerization process
$\lambda_{n=0,1,2}$	zeroth, first and second moment of the growing radicals
$\mu_{n=0,1,2}$	zeroth, first and second moment of the dead polymers

MULTIWAY PARTIAL LEAST SQUARE UNTUK PERMODELAN DAN PENGAWALAN REAKTOR POLY METHYL METHACRYLATE

ABSTRAK

Pempolimeran merupakan proses di mana unit-unit monomer bergabung melalui tindak balas kimia untuk membentuk rantaian monomer yang panjang dipanggil polimer. Proses yang tidaklelurus ini mengeluarkan haba dan pembolehubah keluar seperti berat molekul yang tidak boleh didapati ketika proses sedang beroperasi. Dengan itu ianya perlu diukur melalui analisis makmal dan hanya sampel yang terhad sahaja boleh didapati semasa proses sedang dijalankan.

Ketidakhadiran pembolehubah keluaran seperti berat molekul dan penukaran monomer membawa pada pembangunan model inferensi. Dalam kajian ini model pelbagai cara kuasa dua terkecil separa telah digunakan. Model ini adalah salah satu kaedah Chemometric yang terkenal dimana ianya mampu memantau dan meramalkan pembolehubah keluaran. Model ramalan ini menyediakan tempat dimana pembolehubah keluaran boleh diramalkan berdasarkan data operasi seperti suhu reaktor, suhu jaket dan kadar aliran penyejuk. Model ramalan ini memerlukan sejumlah besar data yang dikumpulkan hasil daripada proses sebelumnya. Proses ini merupakan proses yang dapat menghasilkan keluaran seperti yang dikehendaki.

Dalam kajian ini, ianaya memberi tumpuan kepada ramalan keluar proses pempolimeran seperti penukaran monomer, berat molekul purata dan jumlah berat molekul purata. Ini adalah kerana sifat semulajadi pembolehubah ini yang tidak boleh didapati semasa proses sedang beroperasi. Kajian ini juga membantu untuk memantau pembolehubah di samping mengesan produk di luar spesifikasi. Idea di sebalik model tambahan pula adalah memberikan nilai ramalan pada masa tertentu.

Di samping itu, data-data untuk kajian ini diperolehi melalui simulasi selain daripada loji sebenar ataupun ekperimen. Suhu reaktor, suhu jaket dan kadar aliran penyejuk telah dikenal pasti sebagai pembolehubah masukan manakala berat dan jumlah berat molekul purata serta penukaran monomer digunakan sebagai pembolehubah keluaran. Data simulasi ini telah dianggap sebagai proses yang sebenar.

Model ramalan yang dicadangkan ini telah berjaya meramalkan pembolehubah keluaran dari data pembolehubah masuk yang baru apabila reaktor beroperasi pada suhu 61-64°C. Ramalannya menghasilkan peratusan purata kesilapan yang rendah berbanding suhu di luar julat data pembangunan. Data pembangunan merupakan data yang digunakan untuk membentuk model ramalan. Jika ramalan baru di lakukan ke atas data baru di mana ianya berada di dalam julat data pembangunan, ia juga menghasilkan peratusan kesilapan yang rendah. Model tambahan juga menunjukkan bahawa ianya berjaya meramalkan hasilan pembolehubah keluaran pada masa 150 minit dan 320 minit. Ramalan menghasilkan peratusan yang rendah.

MULTIWAY PARTIAL LEAST SQUARE FOR MODELING AND MONITORING OF POLY METHYL METHACRYLATE REACTOR

ABSTRACT

Polymerization is the process in which monomer units are combined by chemical reaction to form long chains monomer called polymer. The output variables such as molecular weight and conversion are unavailable online thus they need to be measured through laboratory analysis and moreover only a limited sample are made during the process.

The unavailability output variables leads to the development of inferential model which in this study used Multiway Partial least squares (MPLS). MPLS model is one of the famous Chemometric method which able to monitor and predict the process output properties. This inferential model prepared a place where output properties such as molecular weight can be predicted based on operating data such as reactor and jacket temperature and coolant flowrate. This inferential model requires a large amount of data which accumulated during previous processes. These data are considered as normal process which produced desired output properties.

The present study focuses on the prediction the output properties of Methyl Methacrylate (MMA) polymerization such as monomer conversion, the weight average molecular weight (Mw) and the number average molecular weight (Mn). This is due to the nature of these properties since these output properties are not available online. This work helps to monitor the properties and it can be used to detect off specification product. The idea behind the additional model is that this model gives a prediction value at specific time during the process.

Moreover in this study, the properties data were obtained via simulation instead of real plant data or experimental. However, this simulated data were assumed as a real process. Simulated reactor temperature, jacket temperature and coolant flowrate were identified as input variables meanwhile molecular weight (Mw and Mn) and monomer conversion as output variables that been used in MPLS model.

The proposed inferential model was successfully predicts the output properties of new input data at reactor temperature 61-64°C. The predictions gave low average percentage error result compared to the temperatures out of the range of development data. Development data are the data used to build MPLS model. Whenever inputs data was in the range in development data, the percentage error was obviously minimum. The additional model was also successfully predicted the output properties at time 150 minutes and 320 minutes. The errors of predicted output properties were low.

CHAPTER ONE

INTRODUCTION

This chapter firstly covers the introduction of polymerization process and the method of MPLS in predicting and process monitoring. This chapter also provides the objectives, the scope of this research study and lastly thesis organization.

1.1 Introduction

A polymer is a large molecule that is built up by the repetition of small molecules called monomer. This repetition is called polymerization process. Polymer industry is one of the important industries in the world producing the most essential things in our daily lives. Mankind has used polymers since a long times ago such as tyre for vehicle, gloves for protecting hands, footwear for foot protection, rubber-based components and material for transport and construction industries. This industry evolves drastically in chemical industry instead of pharmaceutical, petroleum, food, textile and etc.

Polymer reactor either continuous or batch is designed to produce polymer in wide range of molecular weight. Molecular property is an importance output property to be controlled in order to produce the good and high quality product. This property cannot be measured directly or online thus its need to be measured in the laboratory so that this process needs a delay time to discover its results. The operating conditions in polymer reactor influence the molecular properties of the polymer being produced. Furthermore these properties are difficult to measure frequently because of limited sample.

Polymer producers faced many challenges and the obvious challenge is the heat release by the process reaction. In fact the rapid grow of polymer manufacturer gives an increased demand satisfaction of customer to the end product produce. This creates a dynamic environment where the polymer industries undergo continuous improvement to keep existing in the markets. Thus manufacturers need to concern several aspects such as improve the behaviour of the process, their effect on output properties and efficient process technology. The need to maintain the efficiency of producing the consistent high quality product leads to the development of inferential model.

A big achievement in polymerization reaction engineering is the Chiu et al (1983) model, which this model successfully described the polymerization over entire conversion range based on free volume theory. This model proposed a Methyl methacrylate process model which diffusional limitations affected the rate constants. This model compared to others described the effects of composition, temperature and molecular weight continuously in their model. The other models involved break points to characterize the onset of diffusional limitations.

In chemical process industries, process monitoring and controlling are extremely important in terms of the contribution towards producing a high quality product. Process monitoring plays an important role in current technology as the output of the model is monitor via the prediction based on operational data. Statistical process control (SPC) is effective in monitoring chemical processes and it is applied to monitor and control a process via a prediction chart. In addition it can detect any deviation process via monitoring scheme and the occurrence of off-specification product can also be detected. SPC is a method which uses statistical method in quality control. It is believed that the deviation can be detected and removed more quickly by observing the output properties prediction. In some approach this monitoring process provides acceptable limits where the prediction of the model should lie within this limits. Beside, this process can lead to the identification of unwanted output properties. On top of that this process is able to gives timely information on the process performance and also it helps to reveal the progress of their properties.

This SPC method is a soft sensing tool that has been developed to gives an online measurement of polymer properties. Partial least squares (PLS) and Neural Network (NN) are the famous methods offer that approach. These methods can be modelled by using the historical data of previous processes. NN is similar as MPLS which can make predictions of future data. NN is a software simulation of a biological brain. Its can predict an output pattern when it recognizes a given input pattern. This is different to MPLS, which MPLS consisted equation that can help to predict output data and this method is easy to implement.

Multiway PLS (MPLS) is an extension method of PLS which MPLS generally applied to batch process. Batch process data exist in three dimensional which contains a few batches, variables and time points. In addition, this method is able to handle large volume of data. This method compresses a large volume of data into low dimensional data. MPLS model indirectly describe the process by its low dimensional data of latent structure.

1.2 Problem statement

Producing a consistent high quality product is an objective of all chemical processes especially polymerization process. Producing an intended polymer product is not an easy task as their reactions are nonlinear and highly exothermic. This highly