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Research Article

Comparative Performance of Bootstrap-Optimized Machine Learning Models for Predictive Modeling of Industrial LDPE Production

Anis Farina Mansor[1], Fakhrony Sholahudin Rohman[2],*, Dinie Muhammad[3], Ashraf Azmi[1],*

[1] Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

[2] Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88450 Kota Kinabalu, Sabah, Malaysia

[3] School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia (UTM), 81310 Johor Bahru, Johor, Malaysia

* Corresponding Authors: fakhrony@ums.edu.my; ashraf.azmi@uitm.edu.my

Abstract: This paper presents a bootstrap-enhanced machine-learning framework for predictive modeling of industrial low-density polyethylene (LDPE) production. The high-pressure LDPE tubular reactor is a nonlinear and thermally sensitive process in which operating variables strongly affect reaction temperature, monomer conversion, and melt flow index. A mechanistic reactor model was first used to generate a multiple-input multiple-output dataset through sensitivity analysis of key operating parameters. Three supervised learning models, Gaussian Process Regression (GPR), Support Vector Machine (SVM), and Decision Tree regression, were trained and optimized using bootstrap resampling and grid-search hyperparameter tuning. Model performance was evaluated using the coefficient of determination for three product and process indicators. GPR gave the most balanced performance across all outputs, with R^2 values of 0.9227 for temperature, 0.9261 for monomer conversion, and 0.9246 for melt flow index. SVM produced slightly higher R^2 values for temperature and conversion but performed poorly for melt flow index. Decision Tree regression was less accurate overall but showed acceptable performance for melt flow index. The results indicate that bootstrap-based hyperparameter optimization improves predictive robustness and supports uncertainty-aware surrogate modeling for LDPE process analysis. The revised framework provides a practical basis for future optimization, monitoring, and decision support in high-pressure polymerization systems.

Keywords: Low-density polyethylene; bootstrap resampling; hyperparameter optimization; Gaussian process regression; support vector machine; MIMO modeling

1 Introduction

Low-density polyethylene (LDPE) is an important thermoplastic polymer used in packaging films, tubing, coatings, toys, and electrical insulation because it combines flexibility, chemical resistance, and favourable processing properties. Industrial LDPE is commonly produced through high-pressure free-radical polymerization in tubular reactors. These reactors operate at pressures of approximately 1300 to 3000 atm and temperatures that can approach 330 °C, making safe and accurate process modelling essential [1-4].

The LDPE tubular reactor is difficult to model because polymerization kinetics, thermal effects, and property development are highly nonlinear and tightly coupled. A small change in monomer flow rate, initiator flow rate, jacket temperature, feed temperature, pressure, or solvent flow may alter the temperature profile, monomer conversion, and final polymer quality. Mechanistic models based on

mass and energy balances are useful for process understanding, but their repeated use for data-driven prediction, optimization, and plant-wide decision support can be computationally demanding [4,14-17].

Machine learning provides a complementary modelling route for nonlinear chemical processes. Regression trees are simple and interpretable, SVM models can capture nonlinear relationships using kernel functions, and GPR models provide both predictions and an estimate of uncertainty [5,6,21-25]. However, model performance depends strongly on hyperparameter selection and on the quality of the available data. In industrial LDPE applications, the dataset may be limited, noisy, or obtained from simulation studies rather than direct plant experiments [7-13].

Bootstrap resampling is useful in this context because it creates multiple training subsets by sampling with replacement from the available data. This exposes the learning algorithm to different realizations of the dataset, reduces sensitivity to a single data split, and supports a more stable estimate of predictive performance [13,24]. When combined with grid-search hyperparameter optimization, bootstrap resampling provides a structured way to identify model configurations that are not only accurate but also robust across variations in the training data.

The objective of this study is to compare bootstrap-optimized GPR, SVM, and Decision Tree models for predicting industrial LDPE reactor outputs. The specific aims are to generate a multiple-input multiple-output dataset from a validated LDPE tubular reactor model, optimize the hyperparameters of each model, evaluate predictive performance for temperature, monomer conversion, and melt flow index, and identify the most suitable surrogate model for future LDPE process optimization and monitoring.

2 Materials and Methods

2.1 LDPE tubular reactor model and assumptions

The LDPE reactor was represented using a high-pressure tubular reactor model developed from conservation laws and free-radical polymerization kinetics. The model describes the major reaction pathways that affect initiator decomposition, chain propagation, termination, chain transfer, branching, and polymer property development [14-20]. The reactor model was used as a source of structured data for machine-learning model development rather than as a direct optimization model.

To obtain a tractable industrial representation, the tubular reactor was assumed to operate under ideal plug-flow conditions without axial mixing. The reaction mixture was treated as a homogeneous single phase, pressure variation along the reactor was assumed to be small relative to the inlet pressure, and thermophysical properties were calculated using established correlations [16-19]. The first reaction zone was selected for sensitivity analysis because it represents the region with the strongest temperature and conversion changes.

The input variables and predicted output responses selected for the LDPE surrogate modelling work are summarized in Table 1.

Table 1. Main variables used for LDPE surrogate model development.

Variable group	**Symbol / variable**	**Role in modelling**
Input	FMO	Monomer feed flow rate
Input	FIO	Initiator feed flow rate
Input	Tj, Tp	Jacket and feed temperatures
Input	Pin	Reactor inlet pressure
Input	FSO	Solvent feed flow rate
Output	T	Reactor/product temperature
Output	Xm	Monomer conversion
Output	MFI	Melt flow index

2.2 Sensitivity analysis and data generation

Sensitivity analysis was carried out to generate input-output data for machine-learning model development. Each selected input variable was perturbed from its nominal value using ±5%, ±10%, and ±20% changes. The resulting reactor responses were recorded as temperature, monomer conversion, and melt flow index. This procedure produced a structured MIMO dataset that reflected important operating variations in the LDPE process [19,20].

The sensitivity study focused on identifying how each operating variable affects reactor behaviour. Monomer flow rate and initiator flow rate strongly influenced temperature rise and conversion because they directly affect the reactant supply and radical generation. Temperature-related inputs changed

both kinetic rates and heat release, while solvent flow mainly affected polymer property behaviour. These observations supported the selection of inputs for the machine-learning models.

2.3 Machine-learning model structures

Three supervised regression models were developed: Decision Tree regression, SVM regression, and GPR. Each model used the same input-output structure to ensure a fair comparison. The Decision Tree model divided the input space into interpretable regions and predicted each output using the average response within terminal nodes. It is useful for detecting segmented patterns, although it may be sensitive to small changes in the training data [21].

SVM regression maps the input variables into a higher-dimensional feature space using a kernel function and fits a regression function inside an epsilon-insensitive tube. The hyperparameters considered in this study included kernel function, box constraint, and epsilon value. SVM is attractive for nonlinear processes because the kernel function can represent complex input-output relationships while controlling model complexity [22,23].

GPR is a probabilistic nonparametric model that defines a distribution over possible functions. It predicts the mean response and provides a representation of uncertainty. Three kernel functions were considered: squared exponential, Matern 5/2, and rational quadratic. The best GPR configuration was selected based on predictive accuracy across all three outputs [5,24,25].

2.4 Bootstrap resampling and hyperparameter optimization

Bootstrap resampling was applied to reduce dependence on a single training subset and to improve model stability. For each hyperparameter combination, multiple bootstrap samples were generated by random sampling with replacement. Separate models were trained for the three output variables, and the predictions were averaged across bootstrap iterations. The mean R^2 across the outputs was used to identify the best hyperparameter set [13,24].

The overall bootstrap-enhanced hyperparameter optimization workflow is illustrated in Figure 1.



Figure 1. Bootstrap-enhanced hyperparameter optimization workflow used for LDPE surrogate model development.

2.5 Reproducibility of the modelling workflow

The revised paper was reorganized to make the computational workflow repeatable. The workflow starts from reactor-model implementation, followed by sensitivity-based data generation, input-output normalization, bootstrap sampling, hyperparameter search, model training, prediction aggregation, de-normalization, and performance evaluation. Keeping these steps explicit is important because machine-learning results can vary when data splitting, scaling, or resampling procedures are not fully reported.

For each model family, the same input-output dataset was used. This ensured that the comparison reflected model structure and hyperparameter behaviour rather than differences in data preparation. The model-development procedure also retained the same target variables for all algorithms, namely reactor temperature, monomer conversion, and melt flow index. These outputs represent both process behaviour and product-quality indicators.

To improve transparency, the selected hyperparameters are reported together with the final R^2 values. This allows the study to be repeated using the same model settings and provides a clear basis for future benchmarking with additional algorithms such as Random Forest, gradient boosting, artificial neural networks, or hybrid mechanistic-machine-learning models.

The repeatable computational sequence used for model development and evaluation is summarized in Table 2.

Table 2. Repeatable modelling sequence used in the revised AJPC manuscript.

Step	**Action**	**Purpose**
1	Generate LDPE reactor responses	Create structured data from sensitivity analysis
2	Normalize inputs and outputs	Avoid scale dominance during model training
3	Apply bootstrap resampling	Reduce split dependence and improve robustness
4	Conduct grid-search tuning	Identify stable hyperparameter settings
5	Aggregate predictions	Reduce prediction variance
6	Evaluate R^2 for T, Xm and MFI	Compare models consistently

2.6 Model evaluation

The coefficient of determination, R^2, was used as the main performance indicator because it measures the proportion of output variance explained by the model. For each output variable, R^2 was calculated between the actual simulated response and the predicted response. The final comparison considered both individual output performance and the balance of performance across temperature, monomer conversion, and melt flow index.

The hyperparameter search spaces considered for Decision Tree, SVM, and GPR models are listed in Table 3.

Table 3. Hyperparameter search spaces used in the comparative study.

Model	**Main hyperparameters**	**Candidate values or selected options**
Decision Tree	Minimum leaf size; maximum number of splits; split criterion	{1, 5, 10, 20}; {10, 50, 100, 200}; MSE
SVM	Kernel function; box constraint; epsilon	Linear, Gaussian, polynomial; {0.1, 1, 10}; {0.01, 0.1, 0.5}
GPR	Kernel function; basis function; sigma lower bound	Squared exponential, Matern 5/2, rational quadratic; constant or linear; 1e-2

3 Results and Discussion

3.1 Sensitivity behaviour of the LDPE reactor

The sensitivity analysis showed that the LDPE reactor response is highly nonlinear. Increasing monomer flow rate increased both temperature and monomer conversion in the downstream part of the reactor. However, the improvement in conversion was accompanied by a higher thermal load, which indicates a potential trade-off between productivity and safe operation [19,20,26].

Increasing initiator flow rate also increased the radical concentration, causing earlier temperature rise and higher monomer conversion. This behaviour is desirable for productivity, but excessive initiator addition may produce hot spots and product-quality deviations. These sensitivity results confirm that LDPE operation requires a balanced decision-making framework rather than single-variable adjustment [27-29].

Pressure, feed temperature, jacket temperature, and solvent flow rate had different levels of influence on the outputs. Temperature-related variables directly affected reaction kinetics and heat release. Solvent flow was less strongly correlated with temperature and conversion but remains important for polymer-property regulation. These trends justify the use of a multivariable MIMO prediction framework.

3.2 Comparative performance of machine-learning models

The comparative results show that all three models captured part of the LDPE input-output behaviour, but their reliability differed across output variables. GPR gave the most balanced performance across all outputs. SVM provided slightly higher accuracy for temperature and conversion but showed a large reduction in MFI prediction accuracy. The Decision Tree model was lower overall but performed relatively well for MFI.

The optimized prediction performance of the three machine-learning models is compared in Table 4.

Table 4. Comparative performance of optimized machine-learning models.

Model	**Best hyperparameters**	**R^2 (T)**	**R^2 (Xm)**	**R^2 (MFI)**
GPR	Squared exponential kernel, constant basis, sigma lower bound = 1e-2	0.9227	0.9261	0.9246
Decision Tree	Minimum leaf size = 1, maximum splits = 100, MSE criterion	0.8464	0.8417	0.8995
SVM	Gaussian kernel, box constraint = 10, epsilon = 0.01	0.9313	0.9292	0.6273

The same model-comparison results are visualized in Figure 2 to highlight the R^2 differences across the three LDPE output variables.

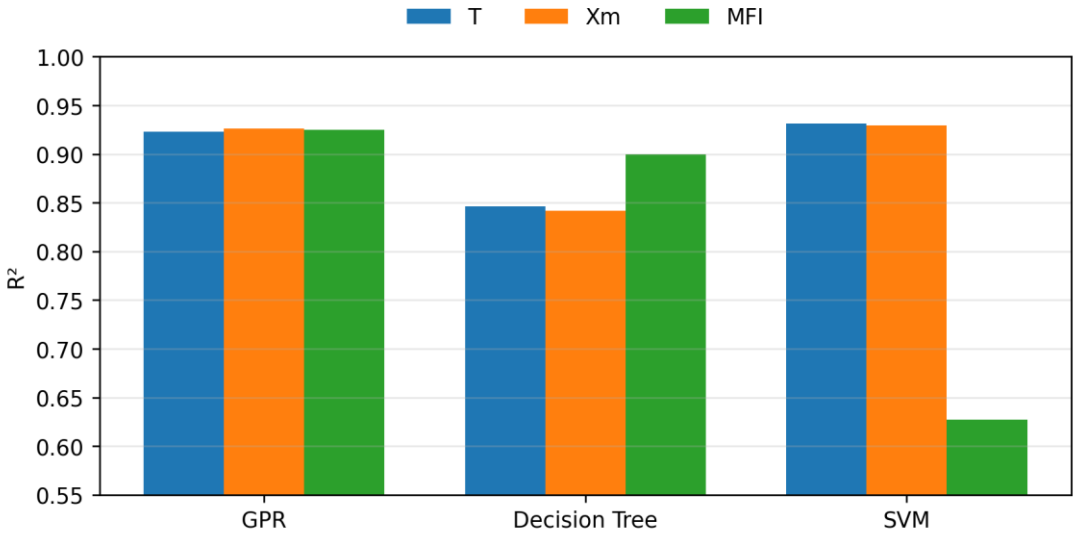


Figure 2. R^2 comparison for temperature, monomer conversion, and melt flow index prediction.

3.3 Gaussian Process Regression performance

GPR achieved R^2 values greater than 0.92 for all three responses. This indicates that the squared exponential kernel and constant basis function provided a stable nonlinear mapping between the selected process inputs and the three LDPE outputs. The balanced performance is important because an industrial surrogate model must predict several quality or process indicators simultaneously.

The probabilistic structure of GPR is also useful for future decision-support work because it can be extended to uncertainty-aware optimization. In LDPE operation, this is valuable because operating decisions must consider both conversion improvement and the risk of unsafe thermal behaviour or off-specification product quality.

The actual and predicted output trends for the GPR model are shown in Figure 3.

3.4 Decision Tree performance

The Decision Tree model achieved lower R^2 values for temperature and monomer conversion than GPR and SVM. This is expected because a single tree partitions the input space into discrete regions and

may not represent smooth nonlinear reactor behaviour as effectively as kernel-based models. Nevertheless, the Decision Tree model gave relatively strong MFI prediction with R^2 = 0.8995.

The acceptable MFI performance suggests that rule-based or segmented relationships may exist in the dataset for this output. This observation motivates future evaluation of ensemble tree methods such as Random Forests or Gradient Boosting, which could retain interpretability while reducing the variance associated with a single tree.

The actual and predicted output trends for the Decision Tree model are shown in Figure 4.

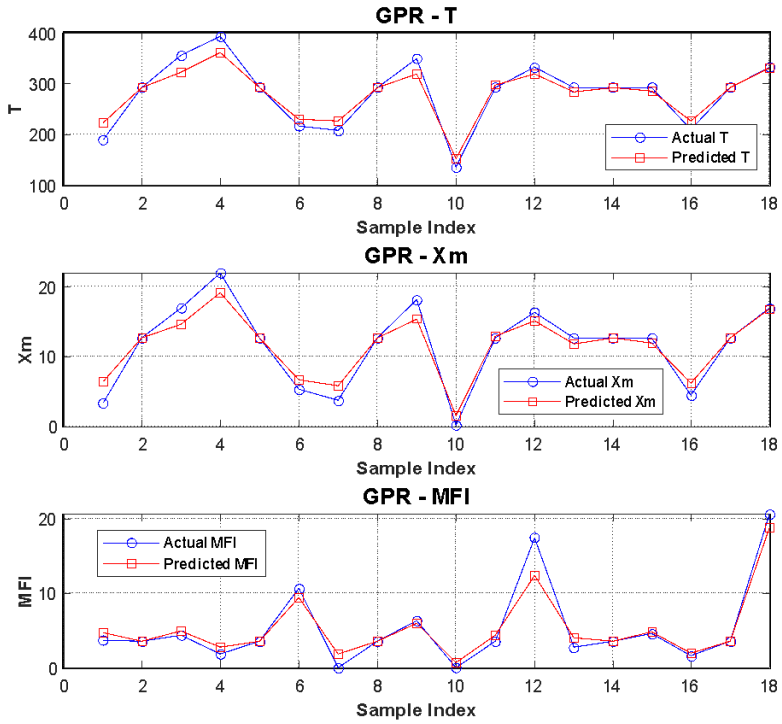


Figure 3. Actual and predicted values for the GPR model.

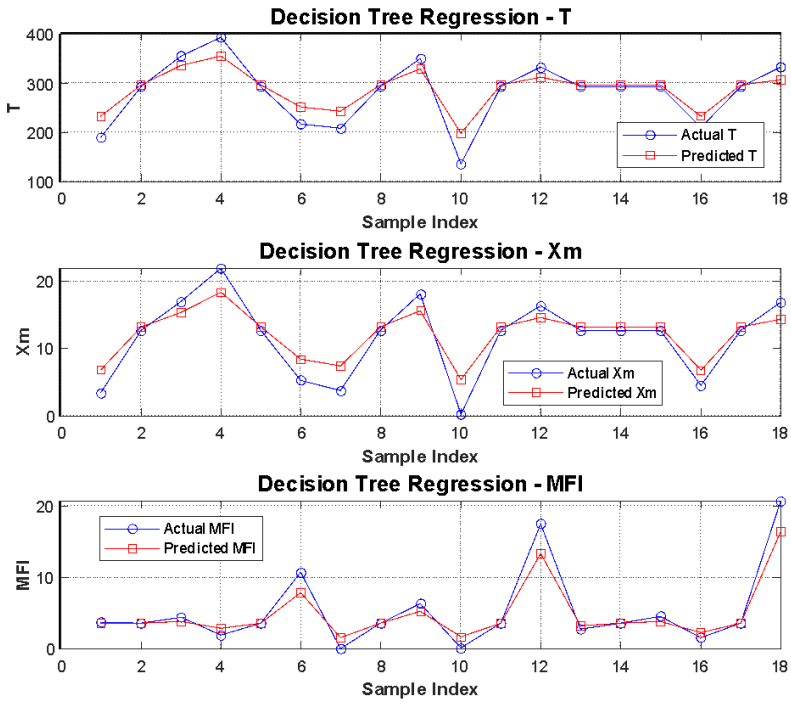


Figure 4. Actual and predicted values for the Decision Tree model.

3.5 Support Vector Machine performance

SVM with a Gaussian kernel achieved the highest R^2 values for temperature and monomer conversion, with R^2 = 0.9313 and R^2 = 0.9292, respectively. This confirms that the Gaussian kernel captured nonlinear relationships in the thermally sensitive outputs. However, SVM performed poorly for MFI, with R^2 = 0.6273.

The reduced MFI performance indicates that a model configuration that is effective for temperature and conversion may not generalize equally well to polymer-property prediction. This reinforces the importance of evaluating all outputs in a MIMO problem instead of selecting a model based only on one variable.

The actual and predicted output trends for the SVM model are shown in Figure 5.

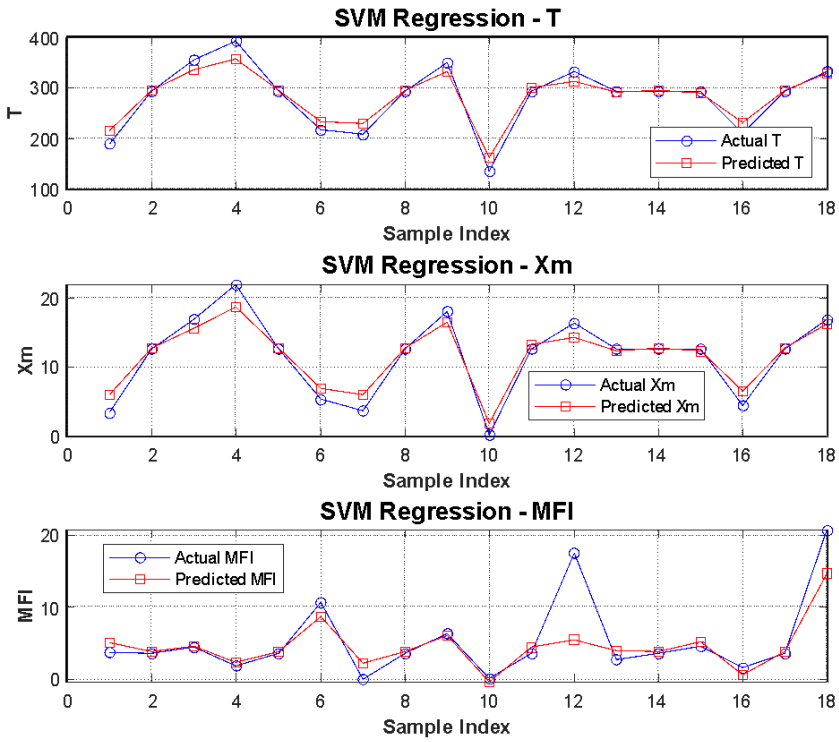


Figure 5. Actual and predicted values for the SVM model.

3.6 Overall comparison and industrial relevance

Overall, GPR is the preferred model because it delivered consistent accuracy for all three outputs. Although SVM gave slightly higher R^2 values for temperature and conversion, its weak MFI result makes it less reliable as a general-purpose MIMO surrogate. The Decision Tree model has value as an interpretable baseline but is not the most accurate option for the full set of outputs.

The bootstrap-based grid-search procedure improved the reliability of model selection by testing each hyperparameter setting across resampled datasets. This is important in industrial LDPE applications because data may be limited and variable. A model selected from a single split can appear accurate but may not be stable under different data compositions.

For practical deployment, the GPR surrogate could be connected to an optimization layer to recommend operating conditions that balance conversion, product quality, and thermal safety. However, the present work should still be interpreted as a surrogate modelling study based on a synthetic MIMO dataset generated from a reactor model. Future validation using plant data is required before direct operational use.

The main strengths and limitations of each model for LDPE production prediction are summarized in Table 5.

3.7 Practical deployment pathway and limitations

The proposed framework can be extended into an industrial decision-support system by connecting the selected surrogate model to an optimization or monitoring layer. In such a system, the mechanistic model or plant historian provides operating data, the GPR surrogate predicts temperature, conversion and MFI, and the decision layer screens operating regions that satisfy productivity and quality targets while avoiding unsafe thermal conditions.

Table 5. Summary of model strengths and limitations for LDPE production prediction.

Model	**Main strength**	**Main limitation**
GPR	Balanced accuracy across all outputs and ability to support uncertainty-aware modelling	Higher computational cost for large datasets
SVM	Strong prediction for temperature and monomer conversion	Weak MFI prediction under the selected configuration
Decision Tree	Simple, interpretable, and relatively good MFI prediction	Less accurate and less smooth for nonlinear reactor behaviour

However, direct deployment requires additional validation. The present work used a synthetic MIMO dataset generated from reactor modelling and sensitivity analysis. While this approach is valuable for systematic comparison, real plant operation may include disturbances, sensor noise, grade transitions, catalyst or initiator changes, and unmeasured operating constraints. Therefore, the model should be validated with independent plant data before it is used for operational recommendations.

The modelling framework also needs uncertainty reporting and model-monitoring procedures during deployment. GPR is attractive because it can provide uncertainty estimates, but these estimates should be calibrated against unseen data. Future work should examine dynamic modelling, online updating, feature selection, and integration with model predictive control or real-time optimization for energy-efficient and quality-consistent LDPE production.

The recommended pathway for future industrial implementation of the proposed framework is summarized in Table 6.

Table 6. Recommended pathway for future industrial implementation.

Stage	**Required work**	**Expected outcome**
Model validation	Use independent plant or high-fidelity simulation data	Confirm prediction robustness
Uncertainty calibration	Compare prediction intervals against unseen data	Support safer decision making
Optimization coupling	Embed GPR in operational optimization	Recommend operating regions
Online monitoring	Track error and model drift	Maintain long-term reliability

4 Conclusions

This study converted a detailed LDPE machine-learning investigation into a compact bootstrap-optimized surrogate modelling framework. A mechanistic LDPE tubular reactor model was used to generate a structured MIMO dataset, and three machine-learning models were compared under systematic hyperparameter tuning and bootstrap resampling.

GPR was identified as the most reliable overall model because it achieved balanced R^2 values above 0.92 for temperature, monomer conversion, and melt flow index. SVM performed slightly better for temperature and conversion, but its poor MFI prediction limited its general suitability. Decision Tree regression performed less consistently but showed useful potential for MFI modelling. These findings highlight the need to select machine-learning models based on all relevant outputs, not only on the best-performing variable.

The main contribution of this work is a practical and uncertainty-aware modelling workflow for LDPE production. The approach can support future process optimization, quality prediction, and decision-support applications. Future work should validate the framework using real plant data, explore ensemble and hybrid models, include additional process features, and extend the method toward dynamic modelling, real-time control, and fault detection.

Declaration of Competing Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

The abbreviations and symbols used throughout the manuscript are listed in Table 7.

Table 7. Abbreviations and symbols used in the revised manuscript.

Term	**Meaning**	**Description**
LDPE	Low-density polyethylene	Polymer product considered in this study
GPR	Gaussian Process Regression	Probabilistic surrogate model
SVM	Support Vector Machine	Kernel-based regression model
MFI	Melt flow index	Polymer quality indicator
Xm	Monomer conversion	Conversion response predicted by the surrogate models
T	Temperature	Thermal response of the reactor
FMO	Monomer feed flow rate	Main reactant feed input
FIO	Initiator feed flow rate	Radical-generation related input
FSO	Solvent feed flow rate	Polymer-property related input
R^2	Coefficient of determination	Model performance indicator

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