

EVOLUTIONARY ALGORITHMS FOR OPTIMAL CONTROL OF PPT POLYMERIZATION REACTOR

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Abstract: Synthesis of Poly(propylene terephthalate) (PPT) is normally carried out (in batch as well as semi-batch mode) in a combined mixture of TPA (terephthalic acid) and PG (1,3-propanediol) with a suitable catalyst in two steps: esterification and polycondensation. Functional group modeling technique is used here to analyse the semibatch PPT formation system. Objectives of multiobjective optimization are to maximize productivity and the proportionality among desired functional groups at minimum possible processing time. But these conflicting objectives lead to an undesired population of other undesired functional groups. Several constraints are incorporated into the system to tackle this situation. Real-coded NSGA-II (Non-dominated Sorting Genetic Algorithm) has been utilized as an evolutionary optimization technique to solve the problem. *Copyright © 2005 IFAC*

Keywords: Polymerization, model validation, poly (propylene terephthalate), multiobjective optimization, optimal control, analysis.

1. INTRODUCTION

PPT has been synthesised (in batch as well as semi-batch mode) with the combination of terephthalic acid and PG with a suitable catalyst (Ti-complex). The process consists of two steps: esterification and polycondensation. Acid-end groups of TPA can catalyze the reaction with an assumption of perfect mixing and constant melt density. This process should be isothermal in nature and normally by-products increase with temperature. Modeling works are not available for PPT in the open literature excepting the recent work by Karayannidis, et al. (2003). With the modeling exercise, Karayannidis, et al. (2003) has done a lot of experiments with different catalysts and ultimately recommended TBOT (tetrabutoxytitanium) as the suitable catalyst. Literature search shows no optimization study for PPT polymerization process till now. A proper

optimization study can have a critical look for the system and many unknown dynamics can come in front, which otherwise is a very tedious task. While performing optimization study, another important issue is maintaining a close proximity with the experimental conditions for which the model is tuned. Otherwise extrapolation error may drive the entire analysis in a wrong direction.

Functional group model is used here to analyse the PPT formation system. Kinetic rate constants are evaluated from the experimental data available in open literature (Karayannidis, et al., 2003). Before optimization analysis, a lot of simulations have been done to see the various dynamics of this polymerization system in batch and semi-batch mode of process. On the other hand, those simulations also help in framing the definition for optimization problem. The main objective of optimization is to maximize the population of desired functional groups. This should lead to the formation of targeted polymer molecule subsequently. Time requirement for the entire process also has to be minimized which should lead to higher productivity. But this

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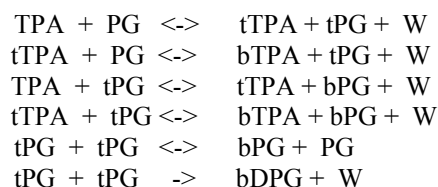
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optimization problem faces a good population of other functional groups as well. Those functional groups are the obvious outcome of the kinetic scheme but at the same time not desired due to the probable increment of poly-dispersity index (PDI) for final polymer latex which may damage the properties of usable polymer. The above stated objectives are conflicting to each other and frame an ideal platform for multiobjective optimization problem (MOOP) for PPT polymerization process. Most of the optimization studies on polymerization reactors involving MOOP use weighted average approach (scalar approach) for solving the same (Deb, 2001). This approach is really inefficient as this not only leads to relatively poor spread in the Pareto set but also requires minimum as many simulation runs as there are distinguished desired points in the Pareto set. Similar fate occurs with ϵ -constraint method when used to tackle MOOPs. Solving MOOPs using a vector of objective functions, where all the objectives are treated simultaneously to find the Pareto set, is reported to be much better approach (Deb, 2001). In the field of traditional optimization, the less robust Pontryagin principle or some other pattern search techniques are often recommended for handling optimization problems dealing with ingredient profiles and enough literature is found on application of the same. Unfortunately, these kinds of traditional optimization techniques require an excellent initial guess of the optimal solutions, and the results and the rate of convergence of the solution are very sensitive to these guesses. For complex systems, quite often, the search space becomes very narrow and one has to provide the initial guess within that narrow region which means one must almost know the optimal solution that one is trying to obtain. In recent years, an extremely robust technique, genetic algorithm (GA) (Goldberg, 1989; Deb, 2001), and its adaptations for more useful but complex multiobjective optimization problems, have become popular. These techniques have the capability of converging to the global optimum even in presence of several local optima. Simultaneously this algorithm is superior to traditional optimization algorithms in many aspects (Deb, 2001). Among several methods (goal attainment method, ϵ -constraint method, versions of nondominated sorting genetic algorithm) available to solve multiobjective optimization problems, nondominated sorting genetic algorithm II (NSGA II), developed by Deb (2001), is used here to obtain the Pareto set. NSGA II, along with a tournament selection based constraint-handling technique, developed by Deb (2000), allows one to get rid of the tuning problem of penalty parameters appearing in penalty function based approaches for handling constraints. Various applications of evolutionary techniques in different chemical engineering problems can be found in the literature (Mitra et al (2004a,2004b), Raha et al (2004), Garg and Gupta (1999), Bhaskar et al. (2000)).

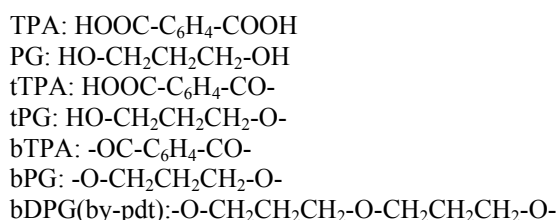
2. PROCESS, MODEL AND OPTIMIZATION PROBLEM FORMULATION

In a lab scale experimental set up (Karayannidis et al., 2003), TPA and PG (propylene glycol) are mixed in a tube with fixed ratio with a catalyst. Temperature for this isothermal process has to be maintained at 260°C under an argon environment and the pressure is atmospheric. Water is normally removed by distillation and collected in a graduated cylinder. This esterification step continues till 74% conversion of TPA (in terms of collected water) has been achieved (Karayannidis et al., 2003). For an isothermal process, polycondensation step is having the same temperature as in the esterification step with a high vacuum. Phosphoric acid has been added and the system is allowed to have a bigger chain length for another 1.5 hours of time. For relevant process issues one can refer Karayannidis et al. (2003).

Table 1: Reaction Scheme for PPT Formation



In the table above, t implies terminal group and b implies repeating unit



The complete kinetic scheme for PPT polymerization process is given in Table 1. The basic guiding equations can be referred to Karayannidis et al. (2003). Namely they are terephthalic acid (TPA), propylene glycol (PG), water (W), TPA end group (tTPA), PG end group (tPG), TPA repeating unit (bTPA), PG repeating unit (bPG) and dipropylene glycol repeating unit (bDPG; by-product). Karayannidis et al. (2003) used functional group approach to develop a batch process model (a system of highly nonlinear-coupled ODE-IVP) based on the kinetic scheme. The “state” of the reactor can be well described by a set of above mentioned 8 state variables, $x = [x_1, x_2, \dots, x_8]^T$. The state variable equations, in general, can be written in the form

$$dx_i/dt = f_i(x); i = 1, 2, \dots, 8; \quad (1)$$

where, x is the vector of the state. These equations are solved by RK-type numerical integration routine (Walas, 1991). The kinetic parameters have been estimated from the available experimental data from Karayannidis et al. (2003). The whole monomer profile is discretized into several points of addition and ingredients to be added at each of this point is treated as decision variables. As time is another decision variable in the first problem, once the

processing time is chosen by the optimization routine, that time is divided into six equal locations and amount of ingredient to be added at those time points are considered as another 14 decision variables (for each of ingredient, there are seven addition points including the amount to be added at the zero hour plus ingredient added for other six time locations). The optimization of monomer profile means finding out optimal values of these parameters (to be searched within given bounds) for which the stated objective is met without violating the constraints. The optimization problem addressed in the present work can be expressed in the standard Nonlinear Programming (NLP) problem as:

Objectives: Maximize DP_n (Objective 1)
 Minimize Time for esterification (Objective 2)
 Minimize Abs |(bTPA/bPG)-1.0| (Objective 3)

Decision variables: [TPA]_i where i=0, 1, 2, ..., n
 [PG]_i where i=0, 1, 2, ..., n
 Polymer processing time

Constraints: Abs |(tTPA/tPG)-1.0| < Value1
 Abs |(total addition of PG/total addition of TPA)-1.2| < Value2
 Total addition of PG < 0.72
 Total addition of TPA < 0.6
 bDPG < Value3 (2)

Values 1 to 3 are some numerical values coming out of large set of simulations and some optimization trials. For this multiobjective optimization problems, real coded nondominated sorting genetic algorithm II (NSGA II), developed by Deb (2001, 2000, 2004), is used here to obtain the Pareto set.

The rationale behind the above optimization problem formulation is as follows:

(1) Maximization of degree of polymerization (DP_n) and proportional growth of the desired functional groups (which is very important for subsequent polymer formation) with the minimization of processing time for esterification step lead to achieving the desired polymer quality with maximum possible productivity; (2) It is assumed that every addition should get a sufficient period of time to establish a perfect mixing mode of operation with the minimizing effects for mass and heat transfer aspects for a reaction controlled process. This is the reason behind selecting a gap of minimum thirty minutes between any two additions of two ingredient profiles. Additionally, as the solubility of TPA is much less in the reaction medium, sufficient time has to be allowed to have a proper dissolution of solid TPA in the reaction mixture; (3) bTPA and bPG should produce proportionately as these two are reacting first to form the basic blocks for polymer repeating units. Same thing is valid for tTPA and tPG, but in this case, they act as end groups and if they are generated proportionately, the major polymer species may look like tTPA-(Repeating Unit)_n-tPG; (4) bDPG is a by-product, so it has to be less than certain specified values, 0.05 mol in this case; (5) Total additions of TPA and PG should not be kept too different from the available experimental conditions of Karayannidis et al. (2003); (6) Basic stoichiometry

with respect to the available experimental conditions (Karayannidis et al., 2003) should be maintained grossly. Experimental evidence shows that ratio of additions of PG with TPA is close to 1.2.

Solubility parameter for TPA in PG is an uncertain data. Solubility value of TPA in PG is very less and its equilibrium solubility value is not available readily. It can be said (Karayannidis et al., 2003) that solubility of TPA can be represented as $\alpha = \alpha_{PG} \cdot W_{PG} + \alpha_{OLIG} \cdot W_{OLIG}$, (α_i = solubility in *i*-th species) where W_{OLIG} is the total weight of all oligomers presented in the reactive medium at any instance and the same for PG is W_{PG} . Solubility value of TPA in PG is assumed to be an arithmetic average value of its solubility in ethylene glycol and butanediol. TPA's solubility value for oligomers is given by Yamada (1996).

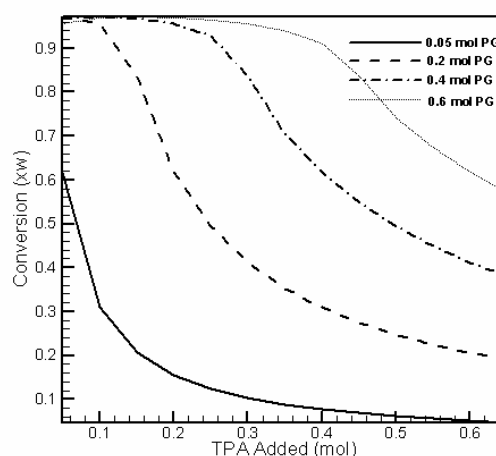


Fig 1: Effects of TPA and PG on the conversion

3. RESULTS AND DISCUSSION

For the process analysis, huge amounts of simulations have been performed to know the dynamic behavior of the PPT polymerization system.

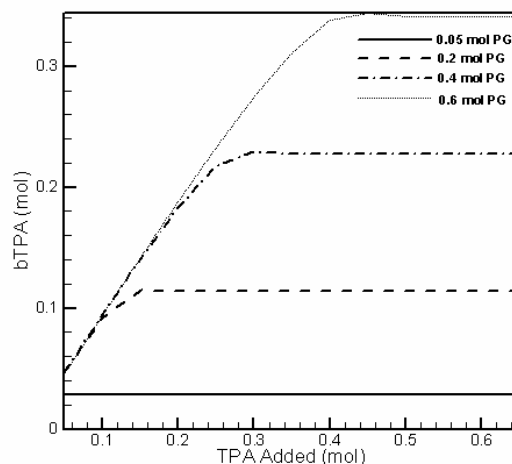


Fig 2: Effects of TPA and PG on the dynamics of bTPA

Figures 1 and 2 show the effects of TPA and PG additions over the different performance parameters of the process. Here all additions have been done in 0-th hour basis i.e. batch mode of operations. Conclusions from different figures are quite contradictory in nature.

Conclusion from Figure 1: For higher conversion of TPA, lower amount of TPA is required with higher amount of PG.

Conclusion from Figure 2: For higher amount of bTPA, higher amount of TPA is required with higher amount of PG.

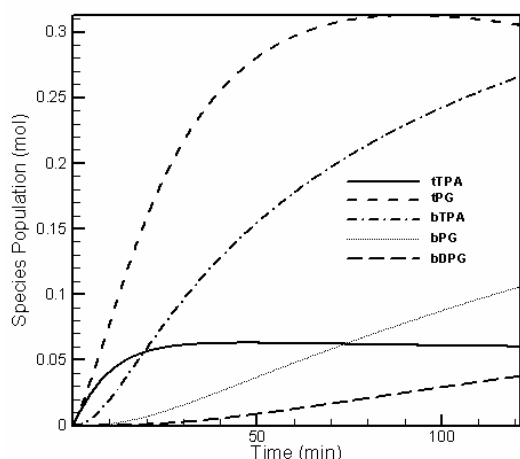


Fig 3: Population of different species for a performance (Time: 121 min; DPn: 2.12)

Not only, conversion and bTPA but also for the other variables like degree of polymerization, bPG, bDPG etc., the respective requirements are highly conflicting. These constitute a difficult optimization problem to be solved. One has to sacrifice some objective to improve other. Here, first an attempt has been made to improve polymer quality rather than substantially decreasing the processing time. If someone stops at early operation, he/ she may find a clear dis-proportionality between the desired functional groups (Figure 3) even for optimized data. This leads towards this present definition of the problem, where minimizing this dis-proportionality is an objective and obviously time frame of processing will substantially increase though there is still an effort to minimize time within given conditions as time is there in the objective function. DPn has also increased substantially compared to earlier observations (DPn was ~2.8; Karayannidis et al. (2003)). Other option to have good proportionality in lower processing time was to allow the more conversion of TPA (more than 74% as used by Karayannidis et al. (2003)). In that case, viscosity will rise stiffly and heat-transfer, fluid mechanics issues will be increasingly important. In this present study, authors tried to stick to ~74% conversion of TPA and efforts have been made to produce good proportionality among desired functional groups. In the present MOOP study, process is completely semi-batch. One can see that with increase in time, the extent of proportionality among bTPA and bPG

is also increasing. It is also interesting to see that all three dimensions are very narrow. Constraints of the MOOP make the search space so narrow that conflicting solutions are only available inside a very narrow feasible domain. Population and proportionality of bTPA and bPG are very critical for the next step of polycondensation, as those will build the basic repeating units for the PPT polymer. To

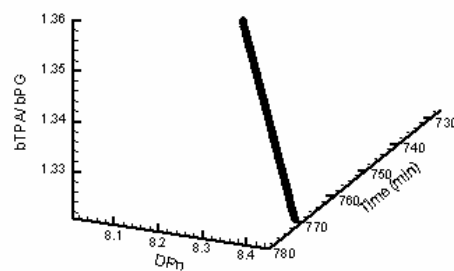


Fig 4: Multiobjective Pareto front for 3-objectives (Objectives: Increase in proportionality among desired functional group, Max. DPn, Min. Time)

verify the claim of having a precise definition, this optimization problem is solved once again with little more allowance of TPA conversion (varying within a range of 74 - 85%). Result is almost similar with Figure 4. This is because, attaining the functional group proportionality in such a conflicting environment doesn't have much choices to operate within a feasible time frame of operation. So, the degrees of freedom with this present optimization definition are much less to allow diversities in operations. Figure 5 shows the optimum comparison for the desired functional groups like bTPA, bPG with the growth of undesired functional group like bDPG. As defined in the optimization definition, bDPG is very less in all the optimized operations, whereas bTPA, bPG are having higher amount of proportionality (~1.3 for the present case). It was seen that if the maximization of proportionality is not considered as an optimization objective, then bTPA/bPG ratio is normally within the range of 2.5 to 3.0.

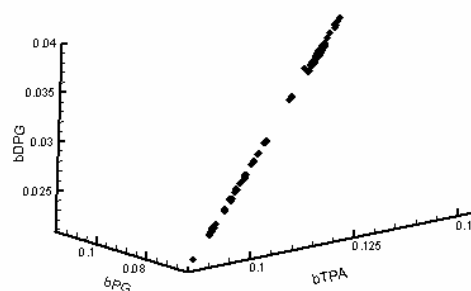


Fig 5: Optimal data for some functional groups corresponding to Figure 4

Additionally, it is worthwhile to present the optimization study, where productivity is taken as a

serious issue and definitely some compromise has been made with the quality of polymer (more disproportionality). Actually, if somebody is more interested in minimizing the processing time at the expense of some quality degradation, he/ she may formulate the optimization problem in the following way:

Objective1: Maximize DPn

Objective2: Minimize Time for esterification

Objective3: Maximize (bTPA+bPG)

Additionally, $|(bTPA/bPG)-1.0|$ has been used as a constraint.

All other constraints are same as earlier. Here time is not a decision variable. Total reaction time is assumed to be 230 minutes. This whole time range is equally divided into 8 divisions of minimum 30 minutes and additions are made at $t = 0, 30, 60, 90, 120, 150, 180, 210$ minutes. So, if repeated for two profiles, this problem has 16 decision variables (amount of ingredient to be added at these time points for two profiles). Each of the simulation run continues till a conversion of 74% is achieved. If conversion is not achieved due to some chosen profiles of TPA and PG, simulation is terminated when the reaction time is reached a value of 230 minutes, as maintained by Karayannidis et al. in their experimental work.

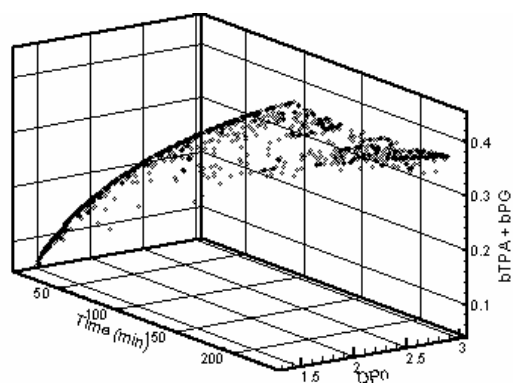


Fig 6: Multiobjective Pareto front for 3-objectives (Objectives: Max. overall generation of desired functional group, Max. DPn, Min. Time)

Figure 6 is showing the resulted Pareto. Processing time is much less here with low DPn value, which indicates dis-proportionality as well as presence of relatively higher amount of bDPG (by-product). One can see that with increase in time DPn is increasing with the increase in (bTPA+bPG) value. This is quite obvious but after a certain time (bTPA+bPG) has come down with saturation in terms of DPn. So the top portion of the multiobjective Pareto front (3D curve) can be a good choice for the operators where one can have reasonable DPn with higher value of (bTPA+bPG) in reasonably less processing time.

For this problem, it has been seen that additions of PG are typically batch and TPA is having a semi-batch mode of addition style for most of the optimized performances. Actually role of PG is dual in nature; it's a reactant as well as it acts as a solvent to TPA specially in the initial period of reaction process. Later half, medium with more oligomers

concentration will be acting as solvent. That is why, higher concentration of PG in the medium is having a critical influence specially over the initial period of reaction process. But for first optimization problem, no distinct feature of this sort is visible. This may be due to the fact that earlier problem definition is talking about much delicate objective function i.e. proportionality instead of overall growth of functional groups. So, more precise control is required over the polyesterification step to produce a good proportionality, which may be extremely difficult for a particular way of additions, especially for a non-linear system with higher conflicts like this. Actually, the effort here was to present a strategy for optimizing a reaction network though one can define his/ her problem formulation to get a target performance out of the PPT polymerization depending on various practical requirements.

The effect of varying GA parameters on the obtained Pareto-optimal front is studied next. If the population size is decreased from 1000 to 500, the convergence rate is marginally faster, but this fastness is achieved at the cost of little poor spread of solutions on the front. The effect of reducing the crossover (from 0.9 to 0.7) and mutation (from 0.1 to 0.01) probability lead to no significant change in converging and maintaining spread of solutions on the Pareto-optimal front. However, when the distribution index of the SBX operator is changed gradually from 0.01 to 100, a slightly inferior spread of Pareto-optimal solutions is obtained. When the distribution index for polynomial mutation operator is changed gradually from 0.01 to 100, a better spread of Pareto-optimal solutions is observed. In all cases, the performance is compared by keeping the same number of overall solution evaluations.

4. CONCLUSION

Esterification step for PPT polymerization has been studied with the help of a functional group based validated model and a state of the art evolutionary optimization technique. Effects of different additions over the process parameters reveal the huge contradictions among the process variables. Optimization study indicates batch mode addition for PG and semi-batch mode for TPA for optimized process performances when optimization drives for more functional groups but scope for optimum operation becomes narrow when quality (in terms of proportionality) has been chosen as an optimization objective. Multiobjective Pareto allows the user to choose a process operating condition from a set of equally competitive non-dominating operating points based on engineering judgements. Due to huge conflicts among variables, betterment of one process objective can only be done at the cost of others.

5. ACKNOWLEDGEMENT

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7. APPENDIX

The GA belongs to the family of optimization techniques that are inspired by living nature (Goldberg, 1989). From the optimization point of view, it represents random search techniques with better capability of searching and capturing a global optimum and has been successfully applied to many problems. It is independent of problem definition, and can converge in cases for which classical techniques have problems of instability or do not converge at all. Contrary to the classical approaches, evolutionary multiobjective optimization (EMO)

procedures aim at finding a finite, representative set of Pareto-optimal solutions in a problem. The task of an EMO procedure is to identify the Pareto-optimal front out of the entire feasible search space. This is, by no means, an easy task. Various optimization concepts must have to be used to clearly identify the true Pareto optimal front. Although one optimal solution would be chosen at the end of the optimization task, a knowledge of the range of Pareto optimal solutions is helpful in (i) choosing a particular optimal solution and (ii) getting useful insights about trade-off among objectives of the problem. Thus, the task of an EMO is to (i) converge to the true Pareto-optimal front and (ii) maintain a good distribution of solutions on the entire front. There exist a number of EMO techniques for this purpose (Deb, 2001). The elitist non-dominated sorting GA or NSGA-II procedure (Deb et al., 2002) for finding a well-distributed and well-converged set of multiple Pareto optimal solutions in a multi-objective optimization problem is described here. Most of the conventional techniques lack in both the qualities described above.

Like in a genetic algorithm (GA), NSGA-II starts with a population of N_{pop} random solutions. In the N th iteration of NSGA-II, the offspring population Q_N is first created by using the parent population P_N and the usual genetic operators—reproduction, recombination, and mutation (Goldberg, 1989). Thereafter, both populations are combined together to form R_N of size $2N_{pop}$. Then, a non-dominated sorting procedure (Deb, 2001) is applied to classify the entire population R_N into a number of hierarchical non-dominated fronts. Once the non-dominated sorting of the set R_N is over, the new population is filled with solutions of different nondominated fronts, one at a time. The filling starts with the best non-dominated front and continues with solutions of the second non-dominated front, followed by the third nondominated front, and so on. Since the overall population size of R_N is $2N_{pop}$, not all fronts may be accommodated in N slots available in the new population. All fronts which could not be accommodated are simply deleted. When the last allowed front is being considered, there may exist more solutions in the last front than the remaining slots in the new population. Instead of arbitrarily discarding some members from the last front, the solutions which will make the diversity of the selected solutions the highest are chosen. In this step, the crowding-sorting of the solutions of front i (the last front which could not be accommodated fully) is performed by using a crowding distance metric and the adequate number of solutions are picked from the top of the list. The crowding distance of a solution in a non-dominated front is a measure of crowding by other members of the front. In the NSGAII implementation, a simple measure totalling the objective wise distances between neighboring solutions is used. For details, readers are encouraged to refer to the original study (Deb et al., 2002). For N population members solving a M -objective problem, the computational complexity of one iteration of NSGA-II is $O(MN^2)$.