

ANALYSING THE START UP OF REACTIVE DISTILLATION COLUMNS

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Abstract: In this paper a simulation model developed for the start up process of a cold and empty reactive distillation (RD) column is presented. The rigorous model is experimentally validated with data from a pilot plant at the department. The sample reaction is a transesterification of a fatty methylester with isopropanol. With the validated model, different start up strategies, known from conventional distillation have been applied. It was found, that the total reflux strategie cannot be recommended for RD processes. Mathematical optimization of the the control variables heating duty, reflux and feed flowrate did not show significant savings in start up time. Alternative strategies utilizing product recycle flows and initial column charges are presented. With these strategies about 80% of the necessary start up time could be saved. *Copyright © 2003 IFAC*

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1. INTRODCUTION

In recent years the integration of reaction and distillation in one process gained industrial and academic interest. The combination of two processes in one piece of equipment can help saving enormous investment and operating costs. The industrial application of reactive distillation processes ranges from esterification (like methyl-, ethyl and butyl acetate) to fuel additives (MTBE, ETBE, TAME) and some alkylations.

With equilibrium limited reactions the thermal separation of the products from the reaction zone can increase the yield of the desired components. Exothermal reaction can contribute to the energy demand of a distillation. This makes reactive distillation a favourable process alternative.

The complexity of the process increases with the interaction of reaction and separation. This requires a better knowledge of the process and the kinetic activities. The steady state process synthesis and simulation for reactive distillation has widely been examined. A comprehensive overview is given by Doherty and Buzad (1992) and Taylor and Krishna (2000).

Exo- and endothermic reactions and changes in feed flows and compositions can have a big impact on the yield in the reactive zone and the required product quality. It is therefore necessary to also analyse the dynamic behaviour of reactive distillation processes, which gained attention just recently. As sample processes the production of acetates with different alcohols were used by Alejski and Duprat (1996) or

Scenna et al. (1998). But these papers all focus on the dynamic behaviour near a known operating point based on a known steady state.

The start up of each distillation column and especially an RD column is a time and energy consuming process. In contrast to distillation without reaction, the off-spec product produced during start up can mostly not be recycled back to the feed stream but most costly be disposed. Also the control of a start up process is very challenging. Almost all process variables change rapidly in value, control variables like heating power, reflux ratio or feed flow have to be switched at least once, but mostly several times to reach steady state. Different start up strategies can yield different, undesired steady states. Processes that show multiplicites and their analysis can be found at Güttinger (1998) and Scenna and Benz (2003). In these papers, the column does not start from a cold and empty state, but from a defined state, with trays filled an warm. To have consisten and physically sound starting values for a process, it is necessary to simulate the complete start up process. In the paper we introduce a rigorous model to simulate the dynamic behaviour of a column from the cold and empty state. The model is validated with experimental data from a pilot plant with a reaction of fatty methylester to isopropylester. Then start up strategies known from conventional distillation are presented and applied to RD. Alternative strategies to minimize the start up time are developed with the aid of the rigorous simulation model.

2. START UP OF REACTIVE COLUMNS

The start up procedure for distillation columns without reaction has already been examined. Kister (1979) describes problems with column start ups. Eden et al. (2000) developed a procedure for generating start up sequences utilizing process knowledge for heat integrated columns. Löwe (2001) developed an optimised strategy for the start up of an energy integrated column system and validated the results. Gani et al. (1987), Gani et al. (1998) published various papers on dynamic simulation of distillation columns with the total reflux strategy. The strategy that is recommended for most of the column start up processes is the total reflux operation.

In the following four strategies that are used are explained and the classifying parameters are explained:

- 1) **Conventional strategy:** The empty and cold column is filled with feed, than all control variables (mainly heating power, reflux rate, feed composition and rate) are set to their steady state values.
- 2) **Total reflux:** The column is filled with feed. Heating begins, if the first distillate reaches the reflux drum, all material is refluxed back into the column. No distillate is taken from the top.
- 3) **Total distillate removal:** during the start up the distillate is completely taken away at the top, there is no reflux stream back into the column.
- 4) **Improved strategy (developed for heat integrated columns):** reflux and reboiler heat duty are set to approximately 1.3 times their steady state value.

The time, where the control variables are switched for strategy 2) to 4) is calculated via the so called MT-function developed by Yasuoka et al. (1987) for distillation without reaction.

$$MT = \sum_{\text{trays}} (T_{\text{tray,current}} - T_{\text{steadystate}}) = \min \quad (1)$$

The MT function is the sum over all trays of the deviations of the actual measured temperature profile to steady state profile, therefore it can be seen as a measure for the distance to steady state. If the function reaches a minimum, the variables should be adjusted to steady state values. With the total distillate removal strategy using the MT function as an indicator for switching, the time for start up of distillation without reaction could be reduced by up to 90% (Kruse et al. (1996); Flender (1999)).

2.1. Modelling and Simulation

To simulate a start up procedure from the cold and empty state to a steady state point a description with just one set of equations is not enough. During the fill up and heating, the trays are not at physical or chemical equilibrium. Therefore it is necessary to have two sets of equations that are active at different

times during the dynamic simulation. The first set is active during the fill up and heating of the column to the boiling point. Once the boiling point of a tray is reached, the second set of equations is activated.

The assumptions made within the overall model are:

- the reaction only takes place in the liquid phase (homogeneous catalysis with sulfuric acid)
- vapour and liquid phase are in phase equilibrium
- vapour phase shows ideal behavior (operation at ambient pressure)

The start up process for a tray is demonstrated in figure 1. In Phase I the tray is empty, cold and at ambient pressure. Feed fills the tray until liquid leaves the stage to the stage below. In phase III vapor from the below stage is entering the stage and heating it up until in phase IV the mixture's bubble pressure reaches the set pressure of 1 bar. The equations are then switched to phase equilibrium. In phase V the stage pressure is higher than the pressure from the stage above, vapor is leaving the stage. In phase VI the stage is operating at steady state. In phases I to IV the first set of equations is active. The switching point is reached exactly if $p_{\text{bub}} = p_{\text{set}}$. Then the phase equilibrium equation is applied.

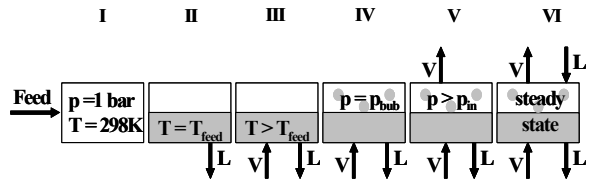


Fig. 1: different states of sample tray during start up

Additionally to the known equations (component, mass and energy balances, Francis weir formula), that are valid from phase I to phase VI, equation 2 and 3 have to be switched if phase IV is reached. For the fill up phase (I-IV), the vapour holdup is set to zero and the vapour compositions are equal to the liquid compositions. Further the pressure is fixed at arbitrarily 1 bar. Once the bubble pressure of the mixture on a tray is reached ($p_{\text{bub}} \geq p_{\text{tray}}$), the equations are switched to

$$M_{\text{Tot,vap}} = 0 \rightarrow V_{\text{tray}} = M_{\text{Tot,vap}} \cdot v^v + M_{\text{Tot,liq}} \cdot v^l \quad (2)$$

$$y_i = x_i \rightarrow y_i \cdot p_{\text{tray}} = \gamma_i \cdot x_i \cdot p_{\text{vap}}^i \quad (3)$$

The reaction rate is captured with a kinetic approach.

$$r_A = k_{\text{for}} \cdot x_A \cdot x_B - k_{\text{back}} \cdot x_C \cdot x_D \quad (4)$$

The sample reaction is a second order reaction from the type $A + B \leftrightarrow C + D$. A detailed listing of the describing equations can be found in Reepmeyer et al. (2003).

2.2. Experimental Validation

For the validation of the rigorous model to simulate the start up of a reactive distillation column from the cold and empty state, experiments with the pilot plant

at TU Berlin have been conducted. As a sample reaction the transesterification of a fatty methyl ester (ME) with isopropanol (IPA) to isopropylester (IPE) and methanol (MeOH) has been chosen. The data of the process are summarized in table 1.

Tab. 1: data for pilot plant at department

number of trays	28	holdup reboiler [l]	5.7
tray holdup [l]	0.3	reflux flow [l/h]	2.3
feed flow ME [l/h]	4	feed flow IPA [l/h]	6
ME temp. [°C]	80	IPA temp. [°C]	130
tray diameter [m]	0.1	tray spacing [m]	0.18

The column has two feeds, one at the top, where the high boiling methylester (ME) is inserted and one at the bottom, where the lowboiling isopropanol (IPA) is prevaporized. Figure 2 shows the comparison of the dynamic temperature profile from the cold and empty state to the steady state point. As can be seen from the figure, the dynamic characteristics of the temperature are well captured. The time were the first vapour reaches the top tray (about 180 mins) can be well predicted by the simulation.

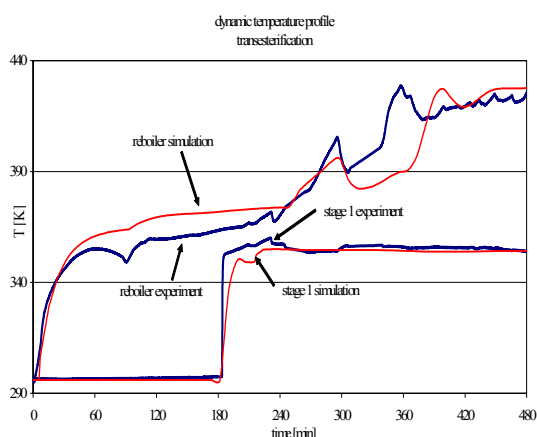


Fig. 2: dynamic validation: experiment vs. simulation for transesterification

But it is important to not only match the temperature profile, but also the dynamic changes in composition to be sure, the precise steady state desired is reached. Especially for RD, the temperature profile is not sufficient to describe a steady state. Therefore during the experiments liquid samples over the column height have been taken. The samples have been diluted with isoocctan and have been analysed with a gas chromatograph. First, the steady state profile over the column height is compared to the simulation data. Figure 3 shows the simulation data in lines and the experimental data in dots. It can be stated, that simulation and experimental data show a pretty good fit. The highest deviation for the reboiler methylester concentration is below 10 mole%.

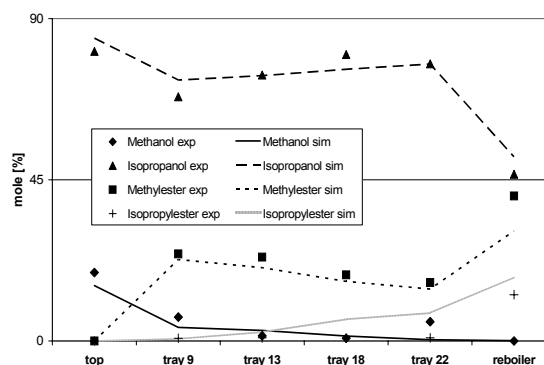


Fig. 3: steady state validation: concentration profile

The following figure 4 shows a comparison of the dynamic concentration profile for simulation and experiment for the reboiler.

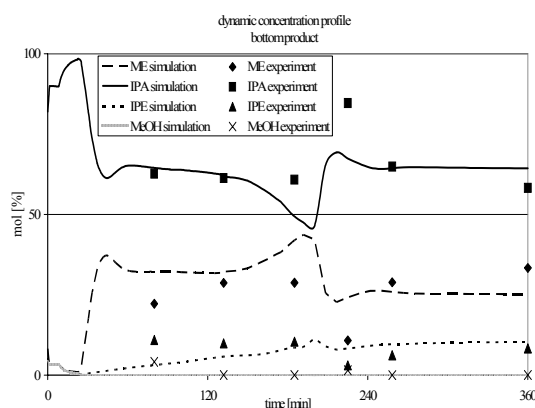


Fig. 4: dynamic validation: concentration profile

As can be seen, the dynamic trend of the concentration is well simulated. The highest deviation between experiment and simulation is 12%. The fit between simulation data and experimental data is satisfactory. It has been shown that the simulated temperature and concentration profiles resemble the experimental data in the steady state as well as in the dynamic start up phase. With this now experimentally validated model, the different start up strategies are calculated.

2.3. Start up times

With the now validated model, start up times for the process are calculated. First the strategies known from distillation without reaction are tested. Table 2 shows the results.

Tab. 2: Comparison of start up times

strategy	start up time [min]
conventional	180
total reflux	260
total distillate removal	182
improved	191

The start up times show, that the strategy of total reflux, recommended for distillation without reaction takes in comparison the longest start up time. The conventional strategy is the best out of these four alternatives.

This sample process of a transesterification has shown, that it is possible to predict the dynamic behavior of a RD start up process with the presented rigorous model. Now the model is applied to a known process, the production of ethyl acetate.

2.4. Ethyl acetate process

The production of ethyl acetate from acetic acid and ethanol has been investigated by several authors like Kenig et al. (2001), Suzuki et al. (1971), Alejski and Duprat (1996) or Lee and Dudukovic (1998). Most of them rely on the following process design.

Tab. 3: ethyl acetate process from Lee and Dudukovic (1998)

number of trays	13	reflux ratio	10
feed tray	6	feed [mol/s]	1.076
diameter [m]	0.6	holdup reb [l]	10
holdup tray [l]	3	weir height [m]	0.05
feed composition (acetic acid, ethanol, water, ethylacetate)	0.4963, 0.4808, 0.0229, 0		

With the model the start up times for this process have been calculated. The following table summarizes the results for the four mentioned strategies.

Tab. 4: start up time: esterification

strategy	start up time [min]
conventional	175
total reflux	225
total distillate removal	183
improved strategy	191

Here the same conclusions can be made as with the transesterification. The total reflux strategy takes the longest time to reach steady state. Therefore it is not suited for reactive distillation processes. The following chapters all base on the esterification as a sample reaction.

3. ALTERNATIVE START UP STRATEGIES

As could be seen from the calculations utilizing the start up strategies for conventional distillation, not much start up time could be saved. Mathematical optimization of the rigorous model, with control variables heating duty, reflux and feed flow and objective function start up time, do not show promise,

because the results would lie between the strategy of total reflux and total distillate removal. Even multiple switching in control parameter sets would not yield significant saving of start up time.

Therefore different procedures have to be developed, starting from different conditions breaking new ground instead of optimizing control variables reflux, heating and feed flow rate. In the following two examples are presented.

- initial charge of the column stages with feed stock, bottom or top product or one reactant in excess
- recycling of top or bottom product during the start up phase

As a measure for reaching the steady state, the MX function for top and bottom product is taken here. The MX function is based on the MT function explained earlier, taking into account the deviation of the top product compositions from the actual point in time to the steady state. The same is done for the bottom product.

$$MX_{Top} = \sum_{\text{components}} \left| (x_{i,top,current} - x_{i,top,steadystate}) \right| \quad (5)$$

If the $MX < 0.01$, the start up period is defined to be finished.

3.1. DIFFERENT INITIAL COLUMN CHARGES

In conventional start up the column is first filled with the feed. Opposite to this, it is possible to charge the column not with feed, but with liquid having a different composition. The following figure 5 shows a simulation of cases for ethyl acetate production with different initial charges. In the diagramm the MX function over time is drawn. Five different charges have been calculated. For the feed composition this is 49.63% acetic acid and 48.08% ethanol, for the top and bottom product it is the steady state composition of the two streams and for acetic acid and ethanol, it is pure educt.

As can be seen from the figure and also from the table showing the start up times, a significant amount of time can be saved, if the low boiler (in this case ethylacetate and ethanol) is initially charged. With pure ethanol as charge, the start up time reduces by 23%, and even more (82%) if the top product is charged to the column. In this column two numbers are listed, because if top product is charged, obviously the MX function for the bottom product takes longer to reach steady state (1.07 h).

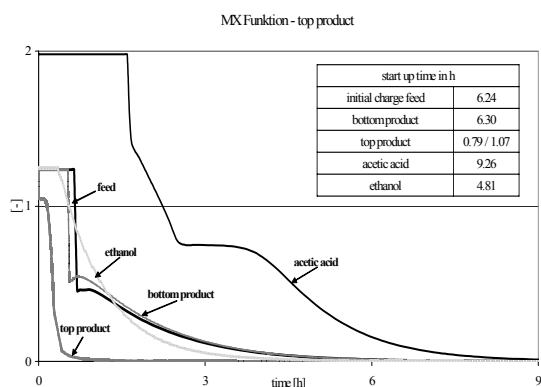


Fig. 5: MX_{Top} function for different initial charges

Therefore it is useful to save some of the top product to recharge the column before the next start up. In the next step a cost optimization has to be executed to see, if the savings in time and off-spec product can compensate the losses in top product. With this significant savings in start up time, the initial charging with top product should be the strategy of choice, if the desired product is the low boiler.

The same set up has been simulated for the transesterification of methylester as in the experiments. Here four different initial charges have been tested. Initially charged with pure methylester and pure isopropanol and charged with bottom product of molar composition ME 52,2%, IPA 34.7%, IPE 12.7% and MeOH 0.4% and with top product of molar composition [0,87.1%, 0, 12.9%]. The required start up times are summarized in the following table

Tab. 5: start up times for initial charges

initially charged with	start up time [h]
pure methylester	5.08
pure isopropanol	5.10
top product	5.23
bottom product	5.27

It can be seen, that the strategy that could save significant amounts of start up time for the ethylacetat process is not the first choice for the transesterification process. The relative volatilities of the products and the kinetics of the reaction have a significant influence in the choice of a sensible start up strategy.

3.2. Recycle of top and bottom product

Another alternative to shorten the start up time of an reactive distillation process is to recycle top and bottom product, that is off spec. This also saves the expensive disposal.

In these simulations, a splitter, that splits the product stream (splitfactor = product/recyclestream) and a

mixer, that mixes the recycle stream with the feed are introduced. The first diagramm shows the recycling of the bottom product with different split factors continuing for different times again for the ethylacetate process.

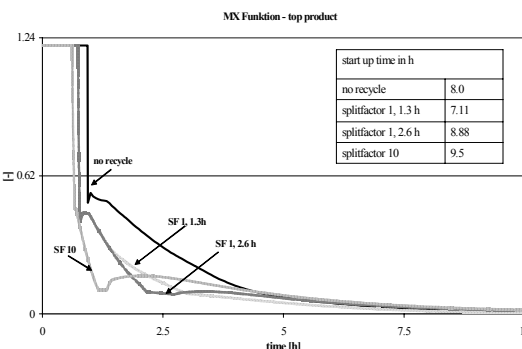


Fig. 6: MX_{Top} function for bottom product recycle

Figure 6 shows, that a moderate recycle of bottom product can save about 12% start up time. A recycle of more bottom product yields a steeper descent of the MX function, but after switching back to regular feed, the MX function shows an increase again, which prolongs the start up time for 1.5 h.

If the top product is recycle, the MX function of the bottom product shows no influence. The start up times for different splitfactors and recycle times do not show significant differences. Therefore this strategy should not be chosen for the start up of a reactive distillation column.

4. CONCLUSIONS

A rigorous simulation model has been presented, that can capture the dynamic behavior of a RD column starting from a cold and empty state. This model has been validated with steady state and dynamic data for a transesterification of a methylester. The match between experimental data and simulation data is satisfactory.

The validated model has been used to calculate start up times for two different processes, one esterification and one transesterification, utilizing strategies known from conventional distillation without reaction. It has been shown, that these strategies do not yield significant savings in start up time. The industrially favoured strategy of total reflux takes the longest start up time for reactive distillation.

Alternative strategies to reduce the necessary start up time have been developed. The investigation of these strategies showed, that a saving of about 82% of the start up time for the ethylacetate process could be achieved, if the column is initially charged with top product. About 23% start up time could be saved, if the low boiling educt is initially charged to the column. Recycling of the bottom product could save about 12% of the start up time whereas a recycling of

top product did not yield in any savings. In contrast to this the transesterification did not show significant start up time reduction for initial top product charging. The relative volatilities of the components as well the kinetic constant are critical for the correct choice of strategies.

5. ACKNOWLEDGEMENT

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6. NOMENCLATURE

D,L,V,B,F	mol/s	Distillate, liquid, vapour, bottom and feed stream
F _V , F _L	mol/sec	vapour, liquid flow
HU _B	mol	liquid holdup
k _{far} , k _{back}	mol/s	frequency factor
K	-	phase equilibrium constant
MT, MX _{Top}		MT function, MX function for top product
M _{Tot,vap} , M _{Tot,liq}	mol	vapour, liquid holdup on tray
p _{vap} ⁱ , p _{tray}	bar	vapour pressure component i, pressure of tray
r _A	mol/s	reaction rate component A
T	K, °C	temperature
V _{tray}	m ³	tray volume
v ^v , v ^l	m ³ /mol	vapour, liquid volume
x _A , x _B , x _C , x _D	mol/mol	liquid mol fraction of components
y _i	mol/mol	vapour mol fraction
Δ _{Level}	m	level of liquid over weir
Δp	bar	pressure drop between two adjacent trays
γ _i	-	liquid activity coefficient

REFERENCES

- Alejski, K. and Duprat, F. (1996). Dynamic Simulation of the multicomponent reactive Distillation. *Chemical Engineering Science*, **51**, pp. 4237-4252
- Bock, H. (1999). Theoretische und experimentelle Analyse der Reaktivrektifikation., VDI Verlag, Düsseldorf, ISBN 3-18-358803-x
- Doherty, M. and Buzad, G. (1992). Reactive distillation by design. *Chemical Engineering Research and Design: Transactions of the Institution of Chemical Engineers: Part A*, **70**, pp. 448-457
- Eden, M., Koggersbol, A. and Hallager, L. (2000). Dynamics and control during startup of heat integrated distillation column. *Computers and Chemical Engineering*, **24**, pp. 1091-1097
- Flender, Matthias (1999). Zeitorientierte Strategien für Anfahr- und Produktwechsellvorgänge an Rektifizierungsanlagen., VDI Verlag GmbH, Düsseldorf, ISBN 3-18-361009-5
- Gani, R., Jepsen, T. and Perez-Cisneros, E. (1998). A generalized Reactive separation Unit Model. Modelling and simulation aspects. *Computers and Chemical Engineering*, **22** (Supp), pp. S363-S370
- Gani, R., Ruiz, C. and Cameron, I. (1987). Studies in the Dynamic of Startup and shutdown Operations of Distillation Columns. *Computers and Chemical Engineering*, pp. 26-30
- Güttinger, T.E. (1998). Multiple Steady States in Azeotropic and Reactive Distillation. Thesis (PhD). ETH Zürich
- Kenig, E.Y., Bäder, H. and Gorak, A. u.a. (2001). Investigation of ethyl acetate reactive distillation process. *Chemical Engineering Science*, **56**, pp. 6185-6193
- Kister, H.Z. (1979). When Tower Startup has Problems. *Hydrocarbon Processing*, **50** (2), pp. 89-94
- Kruse, Ch., Fieg, G. and Wozny, G. (1996). A new time-optimal strategy for column startup and product changeover. *Journal of Process Control*, **6** (2-3), pp. 187-193
- Lee and Dudukovic (1998) Lee, J.-H. and Dudukovic, M.P. (1998). Comparison of the equilibrium and nonequilibrium models for a multicomponent reactive distillation column. *Computers and Chemical Engineering*, **23**, pp. 159-172
- Löwe, K. (2001). Theoretische und experimentelle Untersuchungen über das Anfahren und die Prozessführung energetisch und stofflich gekoppelter Destillationskolonnen., VDI Verlag, Düsseldorf, ISBN 3-18-367803-9
- Reepmeyer, F., Repke, J.-U. and Wozny, G. (2003). Analysis of the Start Up Process for Reactive Distillation. *Chemical Engineering & Technology*, **26**, pp. 81-86
- Scenna, N., Ruiz, C. and Benz, S. (1998). Dynamic simulation of start up procedures of reactive distillation columns. *Computers and Chemical Engineering* (22), pp. S719-S722
- Scenna, N.J. and Benz, S.J. (2003). Start up Operation of Reactive Columns with Multiple Steady States: The Thylene Glycol Case. *Ind. Eng. Chem. Res.* (42), pp. 873-882
- Suzuki, S., Yagi, H. and Komatsu, H. (1971). Calculation of multicomponent distillation accompanied by a chemical reaction. *Journal of Chemical Engineering of Japan*, **4** (1), pp. 26-33
- Taylor, R. and Krishna, R. (2000). Modelling reactive distillation. *Chemical Engineering Science*, **55**, pp. 5183-5229
- Yasuoka, H., Nakanishi, E. and Kunigita, E. (1987). Design of an On-Line Startup System for Distillation Column Based on a simple algorithm. *International Chemical Engineering*, **27** (3), pp. 466-472

