

# EMULSION COPOLYMERIZATION OF ACRYLONITRILE AND BUTADIENE IN A TRAIN OF CSTRs. INTERMEDIATE ADDITION POLICIES FOR IMPROVING THE PRODUCT QUALITY

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**Abstract-** A continuous industrial emulsion copolymerization of acrylonitrile (A) and butadiene (B) carried out in a train of 8 continuous stirred-tank reactors (CSTRs) at 10 °C is theoretically investigated, with the aim of producing nitrile rubber (NBR) of a quality similar to that obtained in an equivalent batch process. The rubber quality is specified by the latex characteristics (number particle concentration and number-average particle diameter), and by the molecular parameters (average values of the copolymer composition, the molecular weights, and the degree of branching). A mathematical model of the NBR industrial batch process is here extended for simulating the operation of the CSTR train. Two NBR grades of a different chemical composition are investigated. Compared with the batch product, the continuous Normal Steady State (SS) operation, with the complete recipe fed into the first reactor of the train, produces a deteriorated rubber (higher polydispersity and higher degree of branching). Such undesirable effects can be corrected through intermediate additions of A and chain transfer agent (CTA) along the continuous train. Finally, the reduction of the off-spec product generated during the change of grade between Normal SSs is also investigated. To this effect, “bang-bang” strategies for the comonomers and the CTA feeds in the first reactor of the train allow reducing up to 30 % of the off-spec product generated when a simple step change in all the feeds is applied.

**Keywords:** Emulsion Copolymerization, Reactor Train, Composition Control, Molecular Weight Control

## I. INTRODUCTION

Nitrile rubber or NBR is industrially produced by polymerizing A and B through the “cold” emulsion process (Kirk and Othmer, 1981). The reaction system can be either a batch (or semibatch) reactor, or a train of CSTRs, when high production levels are required.

The molecular characteristics of NBR are mainly determined by the copolymer composition, the molecular weights, and the degree of branching. The most common NBR grade (BJLT) contains a total mass fraction of bound A ( $\bar{p}_A$ ) of about 35%. This value is

slightly lower than the azeotropic composition of 38% (Ambler, 1973), and therefore a moderate compositional drift along the reaction is normally observed. The CJLT grade is closer to the azeotrope, and for this reason  $\bar{p}_A$  is practically uniform. The AJLT grade has a  $\bar{p}_A$  value of about 20%, and it exhibits an important compositional drift that produces a deteriorated rubber with multiple glass transitions (Guyot *et al.*, 1984). Many composition control strategies have been developed. For instance, Vega *et al.* (1997) controlled the compositional drift of a BJLT grade through a semibatch policy that considered impulsive additions of A along the reaction.

The molecular weights are usually limited by adding a chain transfer agent (CTA) in the reaction recipe (Ambler, 1973). Also, the degree of branching is maintained under 1 branch per molecule by limiting the final conversion to around 75%. While the number-average molecular weight ( $\bar{M}_n$ ) remains practically constant, both the weight-average molecular weight ( $\bar{M}_w$ ) and the average number of trifunctional branches per molecule ( $\bar{B}_{n3}$ ) increase along the reaction, producing a higher final polydispersity.

Mathematical models of the NBR emulsion process for predicting the average molecular properties ( $\bar{p}_A$ ,  $\bar{M}_n$ ,  $\bar{M}_w$ ,  $\bar{B}_{n3}$ ) have been reported by Dubé *et al.* (1996), Vega *et al.* (1997), and Rodríguez *et al.* (2002). The model by Vega *et al.* (1997), has been recently applied for estimating conversion and average molecular properties, on the basis of calorimetric measurements taken in a semibatch industrial process (Gugliotta *et al.*, 1999; Vega *et al.* 2002). In Vega *et al.* (2002) control strategies were developed for producing NBR with predetermined profiles of copolymer composition and average molecular weights.

Several articles have investigated the optimization and control of a CSTR train for the production of styrene-butadiene rubber (SBR), but the problem of the continuous production of NBR has not yet been addressed. For the SBR process, Vega *et al.* (1995a) and Minari *et al.* (2006) improved the polymer production by splitting the comonomers mixture feed into the first reactors of the train. Also, they control the final quality properties by intermediate SS additions of CTA. While Vega *et al.* (1995a) imposed a constant

$\bar{M}_n$  profile along the train, Minari *et al.* (2006) aimed at controlling  $\bar{M}_n$ ,  $\bar{M}_w$ , or  $\bar{B}_{n3}$  profiles. These last authors found that the best final properties were obtained when controlling  $\bar{M}_w$ .

In industrial practice, the changes of grade are rather frequent, for which reason a large amount of off-spec product is generated during the transients. Vega *et al.* (1995b) and Minari *et al.* (2006) considered reducing the off-spec SBR during changes of grade. The off-spec product was only defined on the basis of average values of the molecular weights and the degree of branching, because the copolymer composition was practically constant. Vega *et al.* (1995b) considered the plant policies for reducing off-specs, which involved “bang-bang” profiles of the initiator and/or the CTA feeds into the first reactor. As far as the authors are aware, there is not previous articles that investigated the change of grade involving simultaneous transition of the molecular weights, the degree of branching and the copolymer composition.

This theoretical work investigates the production of NBR in an industrial CSTR train, with the aim of obtaining a final product exhibiting the same quality properties of the batch operations. Also, the off-spec reduction during the change of grade between Normal SS operations was investigated.

## II. MATHEMATICAL MODEL AND BATCH PROCESS

The model by Vega *et al.* (1997) for the semibatch emulsion copolymerization of A and B is here employed for simulating the batch reactions, and extended for simulating the SS operation of the CSTR train. The model considers: a) the particle nucleation via micellar and homogeneous mechanisms; b) the distribution of monomers and CTA between the phases according to equilibrium; c) the desorption of primary A radicals from the polymer particles; d) the homopolymerization of A in the aqueous phase; and e) the effect of impurities such as oxygen and vinyl acetylene. The kinetic scheme involves reactions in both the aqueous phase (redox initiation, propagation of A, radical deactivation and  $\text{Fe}^{2+}$  oxidation by  $\text{O}_2$ , and termination of polyacrylonitrile radicals), and in the polymer phase (propagation, chain transfer to comonomers, CTA and polymer, reactions with internal double-bonds and with impurities). The model predicts the evolution of the monomer conversion,  $x$ ; the

number-average particle diameter,  $\bar{d}_p$ ;  $\bar{p}_A$ ;  $\bar{M}_n$ ;  $\bar{M}_w$ ; and  $\bar{B}_{n3}$  along the train. The physicochemical parameters applied by Vega *et al.* (2002) are here employed for simulating both batch and continuous reactions.

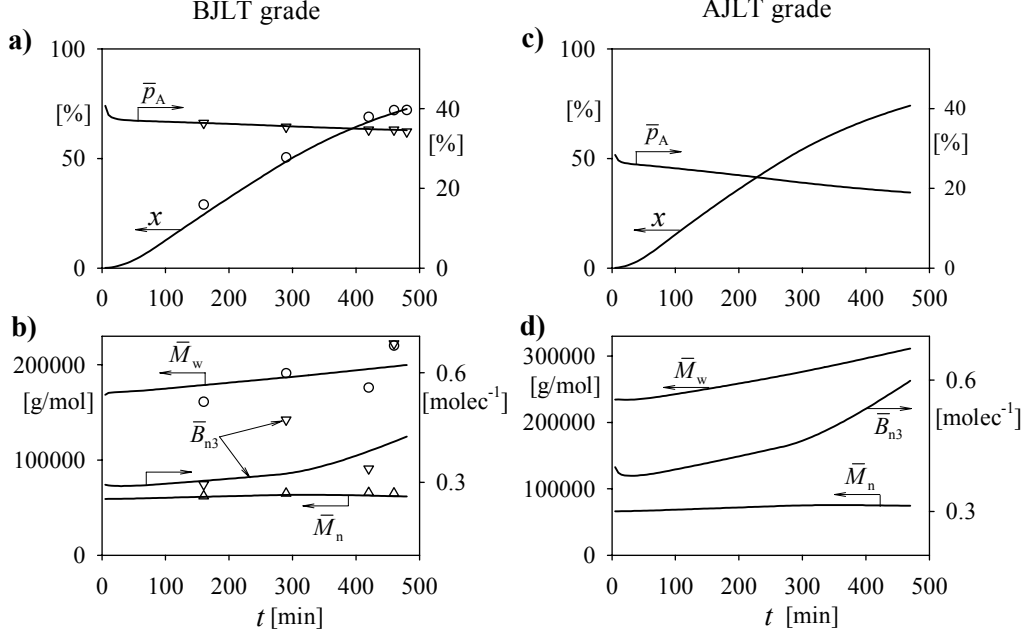
Consider first the batch emulsion process for the production of grades BJLT and AJLT. The recipes of the two investigated reactions are presented in the upper section of Table 1. The synthesis of grade BJLT was carried out at 10 °C in a 21000 L industrial reactor, property of Petrobras Energia S.A. (Pto. Gral. San Martín, Santa Fe, Argentina). The production of grade AJLT was only simulated, applying identical reaction conditions. The model predictions for the final rubber properties are given in the lower section of Table 1.

Figure 1 presents the simulated evolutions of  $x$ ,  $\bar{p}_A$ ,  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{B}_{n3}$ . The experimental measurements for the BJLT grade are represented by symbols in Fig. 1a,b), and were taken from Vega *et al.* (2002). The main variables follow similar evolutions, independently of the grade, with an almost uniform  $\bar{M}_n$  along the reaction. The AJLT grade exhibits a higher drop in  $\bar{p}_A$ ; and a larger increase in  $\bar{M}_w$ ,  $\bar{M}_w/\bar{M}_n$ , and  $\bar{B}_{n3}$ .

**Table 1.** Recipes and product properties of the simulated batch reactions.

NBR Grade	BJLT	AJLT
A [pphm] <sup>(1)</sup>	31.7	15.0
B [pphm]	68.6	85.0
Water [pphm]	170.2	170.2
Emulsifier [pphm]	3.488	4.185
Initiator [pphm]	0.0027	0.0046
CTA [pphm]	0.4086	0.3000
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$x$ [%]	72.67	74.13
$\bar{d}_p$ [nm]	69.5	57.7
$N_p/V_w \times 10^{-18}$ [L <sup>-1</sup> ]	2.456	4.374
$\bar{M}_{n,b}$ [g/mol] <sup>(2)</sup>	61650	74590
$\bar{M}_{w,b}$ [g/mol]	199700	311400
$\bar{M}_{w,b}/\bar{M}_{n,b}$ [dimensionless]	3.24	4.17
$\bar{B}_{n3,b}$ [molecule <sup>-1</sup> ]	0.4252	0.5983
$\bar{p}_{A,b}$ [%]	34.6	18.9

<sup>(1)</sup> pphm: parts per hundred monomers (given on a weight basis); <sup>(2)</sup> subscript b indicates batch operation



**Figure 1.** Batch polymerizations (BJLT and AJLT grades). For the BJLT grade, the experimental measurements are indicated by symbols (after Vega *et al.*, 2002). (a, c) Gravimetric conversion and mass fraction of A in the copolymer. (b, d) Average molecular weights and average number of trifunctional branches per molecule.

### III. CONTINUOUS OPERATION OF THE CSTR TRAIN

Consider the continuous production of NBR in a train of 8 CSTRs (property of Petrobras Energía S.A.). All the reactors have a reaction volume of 17473 L, and are operated at a constant temperature of 10 °C. We aim at producing a rubber with the same final values of conversion, latex characteristics, and macromolecular properties, as in the previously-described batch reactions.

#### A. Normal Steady State Operation

In the Normal SS operation, all the reagents are fed into the first reactor. The same recipes of the batch reactions are used. If the total volume feed rate into the train,  $q_T$ , is selected to produce a total mean residence time equal to the batch reaction time, then lower final conversions are obtained. To avoid this problem, the initiator recipe and  $q_T$  were simultaneously adjusted for reaching the final batch polymerization values of  $x$ ,  $\bar{d}_p$  and the ratio  $A_E/A_p$  (i.e., the particle area covered by the emulsifier with respect to the total particle area, which gives information on the latex stability.)

For both grades (BJLT and AJLT), the reaction conditions and the Normal SS results are shown in the third and sixth columns of Table 2, and compared with conditions and simulation results corresponding to the batch operation. The following performance index is proposed to quantify a global average error of the final quality properties, when changing from the batch to the continuous operation:

$$J = \frac{|\bar{M}_w - \bar{M}_{w,b}|}{\bar{M}_{w,b}} + \frac{|\bar{M}_n - \bar{M}_{n,b}|}{\bar{M}_{n,b}} + \frac{|\bar{M}_w / \bar{M}_n - \bar{M}_{w,b} / \bar{M}_{n,b}|}{\bar{M}_{w,b} / \bar{M}_{n,b}} + \frac{|\bar{p}_A - \bar{p}_{A,b}|}{\bar{p}_{A,b}} + \frac{|\bar{B}_{n3} - \bar{B}_{n3,b}|}{\bar{B}_{n3,b}} \quad (1)$$

Each term of Eq. (1) evaluates the relative error between the final average value of a molecular characteristic and its corresponding batch operation value (indicated by the subscript b). The differences in absolute value are evaluated because any modification with respect to the batch results deteriorates the NBR quality. In the case of  $\bar{B}_{n3}$ , however, an improvement of the polymer quality by reduction of this property is admitted. Due to the important effect of polydispersity on the polymer quality, the third term of Eq. (1) was included to penalize high errors in  $\bar{M}_w / \bar{M}_n$  originated by small opposite errors in both  $\bar{M}_n$  and  $\bar{M}_w$ .

For both grades, the following can be noted in the Normal SS: i) for obtaining  $x$ ,  $\bar{d}_p$ , and  $A_E/A_p$  as in the batch operation, the initiator recipe must be higher than the batch, with  $q_T = 321.72$  L/min (=85 gal/min); ii) even though  $\bar{M}_n \cong \bar{M}_{n,b}$ , the final product exhibits a deteriorated quality with respect to the batch ( $\bar{M}_w > \bar{M}_{w,b}$ ,  $\bar{B}_{n3} > \bar{B}_{n3,b}$ , and  $\bar{M}_w / \bar{M}_n > \bar{M}_{w,b} / \bar{M}_{n,b}$ ); and iii) the consumptions of A and CTA per unit mass of NBR (indicated as  $\sum_r F_A^{(r)} / G$  and  $\sum_r F_X^{(r)} / G$  in Table 2) are similar to the batch consumptions.

**Table 2.** Operating Conditions and Final Properties for the Investigated Operations.

	BJLT grade			AJLT grade		
	Batch Operation	Normal SS	SS1	Batch Operation	Normal SS	SS2
$q_T$ [L/min]	----	321.7	321.7	321.7	359.5	359.5
Initiator [pphm]	0.0027	0.0095	0.0095	0.0046	0.0156	0.0156
$G^{(a)}$ [Kg/min]	----	72.21	73.43	----	72.70	73.50
$\sum_r F_A^{(r)}/G^{(b)}$	0.432 <sup>(c)</sup>	0.438	0.449	0.202	0.204	0.208
$\sum_r F_X^{(r)}/G^{(b)}$	$5.6 \times 10^{-3}$ <sup>(c)</sup>	$5.7 \times 10^{-3}$	$6.2 \times 10^{-3}$	$4.0 \times 10^{-3}$	$4.1 \times 10^{-3}$	$4.5 \times 10^{-3}$
$x$ [%]	72.67	72.67	73.62	74.13	74.15	74.58
$\bar{d}_p$ [nm]	69.50	69.49	69.49	57.70	58.12	58.21
$N_p/V_w \times 10^{-18}$ [L <sup>-1</sup> ]	2.456	2.480	2.480	4.374	4.296	4.322
$\bar{M}_n$ [g/mol]	61,650	61,010	58,230	74,590	74,740	69,800
$\bar{M}_w$ [g/mol]	<b>199,700</b>	210,100	<b>199,700</b>	<b>311,400</b>	349,000	<b>311,400</b>
$\bar{M}_w/\bar{M}_n$	3.24	3.44	3.42	4.174	4.669	4.458
$\bar{B}_{n3}$ [#molecule]	0.425	0.467	0.453	0.598	0.642	0.604
$\bar{p}_A$ [%]	<b>34.6</b>	34.8	<b>34.6</b>	<b>18.9</b>	18.7	<b>19.0</b>
$A_E/A_p \times 100$ [%]	47.21	47.21	46.79	47.34	47.73	47.55
$J$	0	0.232	0.163	0	0.323	0.152

(a) polymer production; (b) consumption of A (or CTA) per unit mass of NBR; (c) ratio between the initial charge of A (or CTA) and the total mass of NBR produced under batch conditions.

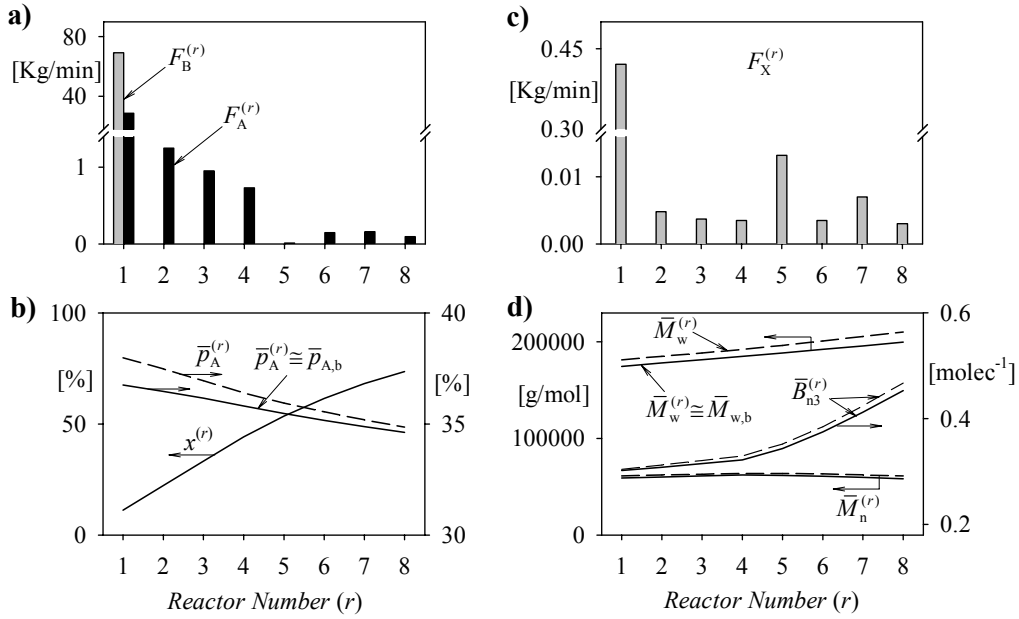
## B. Control of Molecular Properties

The deterioration of the rubber quality is a consequence of the relatively broader residence time distribution of the train with respect to the batch. More specifically, in the train there is a higher probability of reactions with the accumulated polymer (transfer to the polymer and reactions with internal double-bonds), and this produces increased polydispersities and branching degrees. To correct for this problem, the intermediate addition of the comonomers and the CTA along the train is proposed.

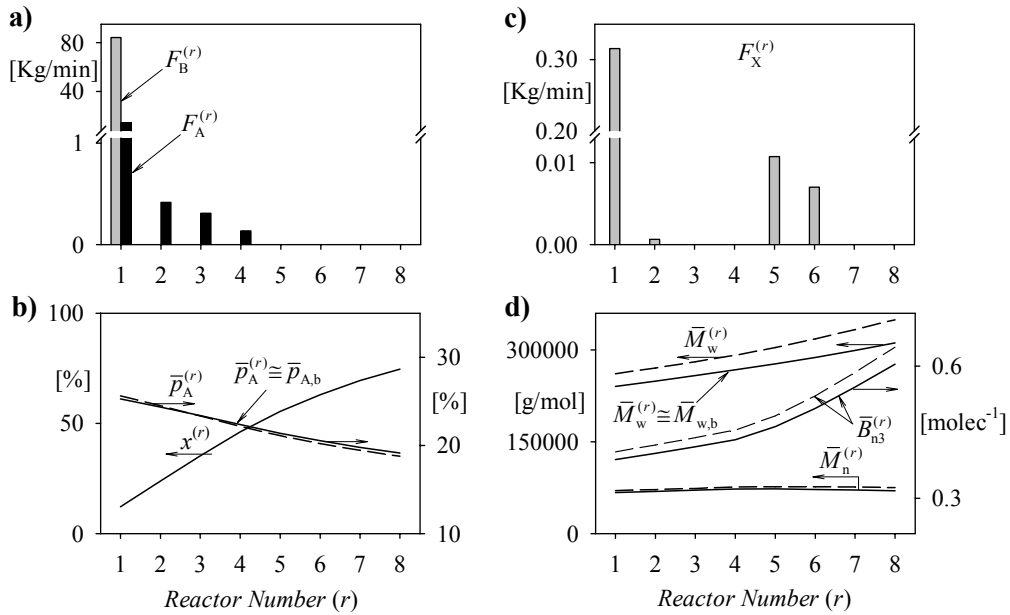
The CTA concentration importantly affects  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{B}_{n3}$ , but it has a negligible influence on the copolymerization rates and on  $\bar{p}_A$ . Thus, it is possible to control the average molecular weights and branching by manipulating the CTA addition without affecting conversion and copolymer composition. This is rather fortunate, since it is then possible to calculate the improved SSs in two sequential steps. In the first step, the comonomer feeds are calculated to produce a prespecified profile of  $\bar{p}_A$  (see Appendix A). In the second step, the CTA feeds are estimated with the aim of obtaining a prespecified profile of either  $\bar{M}_n$ ,  $\bar{M}_w$ , or  $\bar{B}_{n3}$  (Minari *et al.*, 2006). Unfortunately however, it

is impossible to simultaneously control  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{B}_{n3}$ .

In what follows, intermediate SS additions of A and CTA are manipulated for reproducing the batch profiles of  $\bar{p}_A$  and  $\bar{M}_w$ ; while all other feeds are maintained as in the Normal SS. The simulation results corresponding to this improved SS operation (SS1 for BJLT grade and SS2 for AJLT grade) are shown in Table 2 and Figs. 2 and 3. Note the following: i) in all reactors  $\bar{p}_A \cong \bar{p}_{A,b}$  and  $\bar{M}_w \cong \bar{M}_{w,b}$ ; ii) the monomer conversion is 1% higher than the batch conversion; and iii)  $\bar{M}_n$  is somewhat lower than  $\bar{M}_{n,b}$  in all the reactors, with the final  $\bar{M}_n$  around 6% lower than the batch; and iv) both the final polydispersity and the branching degree are higher than in the batch. However, the NBR properties are better than those of the Normal SS, with a lower value of  $J$ , but with higher consumptions of A and CTA (around 2.5% and 9.5% respectively). Even though not shown for reasons of space, the product obtained under  $\bar{M}_w$  control exhibits better qualities (and lower values of  $J$ ) than the NBR obtained under the control of either  $\bar{M}_n$  or  $\bar{B}_{n3}$ .



**Figure 2.** Improved SS operation for BJLT grade (SS1) obtained after imposing the batch profiles of  $\bar{p}_A$  and  $\bar{M}_w$ . (a, c) A and B feed profiles. (b, d) Conversion and copolymer composition. For comparison, the equivalent Normal SS results are also presented (in dashed trace).



**Figure 3.** Improved SS operation for AJLT grade (SS2) obtained after imposing the batch profiles of  $\bar{p}_A$  and  $\bar{M}_w$ . (a, c) A and B feed profiles. (b, d) Conversion and copolymer composition. For comparison, the equivalent Normal SS results are also presented (in dashed trace).

#### IV. CHANGES OF GRADE

Consider the minimization of transient during the changes of grade (BJLT $\leftrightarrow$ AJLT) between Normal SS. The transition involves a modification in all the recipe for an identical total feed rate, with relatively small changes in the polymer production. The analyzed grades exhibit different average values of molecular weights, degree of branching, and copolymer composition. For example, during the change

BJLT $\rightarrow$ AJLT,  $\bar{p}_A$  decreases, while  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{B}_{n3}$  increase (see third and sixth columns of Table 2)].

In the industry, the intermediate off-spec is obtained when the product exhibits Mooney viscosity or copolymer composition out of specification. In this work, we considered that the final product is out of specification when any of its molecular properties ( $\bar{p}_A$ ,  $\bar{M}_n$ ,  $\bar{M}_w$ ,  $\bar{M}_w/\bar{M}_n$  or  $\bar{B}_{n3}$ ) fall outside the specification band of some grade. For  $\bar{M}_n$ ,  $\bar{M}_w$ ,

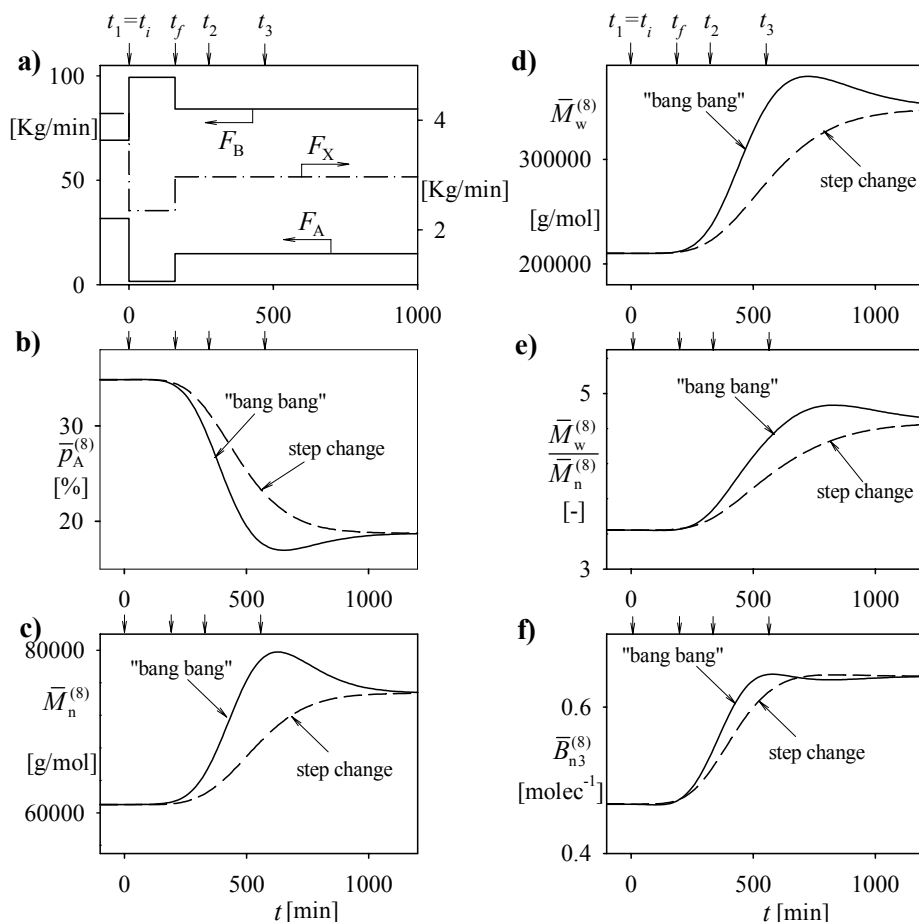
$\bar{M}_w / \bar{M}_n$  and  $\bar{B}_{n3}$ , we adopted  $\pm 10\%$  of their SS values as bands of specification, and for  $\bar{p}_A$  the grade specifications were considered, [ $\bar{p}_A \pm 2.5\%$ ] for BJLT and [ $\bar{p}_A \pm 2\%$ ] for AJLT.

For reducing the off-spec product we propose to manipulate the comonomers feeds ( $F_A$  and  $F_B$ ) and the CTA feed ( $F_X$ ) in the first reactor, by means of a “bang-bang” strategy with an intermediate period where: i)  $F_X$  presents a minimum when the molecular weights increases; ii)  $F_A$  presents a maximum when  $\bar{p}_A$  increases; and iii)  $F_B$  is manipulated to maintain constant the total mass feed of comonomers  $F_B + F_A$ .

The proposed strategy is as follows: a) at  $t=t_1=0$ , the initiator and the emulsifier feeds are changed to the values of the final grade; b) at  $t=t_i$ , a “bang-bang” profile to  $F_A$ ,  $F_B$ , and  $F_X$  is applied; and c) at  $t=t_f$ ,  $F_A$ ,  $F_B$ , and  $F_X$  are changed to the feeds corresponding to the final grade. The values of  $t_i$ ,  $t_f$  and the applied variation in  $F_A$ ,  $F_B$  and  $F_X$  were optimized with the

objective of minimizing the total off-spec product.

The results of the transition BJLT→AJLT between Normal SSs are shown in Fig. 4. Figure 4.a) presents the manipulated feed profiles ( $F_A$ ,  $F_B$ , and  $F_X$ ), where: i) at  $t=0$ ,  $F_X$  and  $F_A$  are reduced 43% and 95%, respectively ( $F_B$  is manipulated with the objective of maintaining constant  $F_B+F_A$ ); and ii) at  $t_f=160$  min,  $F_A$ ,  $F_B$ , and  $F_X$  are changed to the values of the AJLT grade. Figs. 4.b-f) present (in solid line) the evolution of  $\bar{p}_A^{(8)}$ ,  $\bar{M}_n^{(8)}$ ,  $\bar{M}_w^{(8)}$ ,  $\bar{M}_w^{(8)} / \bar{M}_n^{(8)}$ , and  $\bar{B}_{n3}^{(8)}$ , respectively. For the proposed strategy, the off-spec are accumulated between  $t_2=280$  min (when  $\bar{p}_A^{(8)}$  is the first variable out of the specification bands of the initial grade) and  $t_3=470$  min (when  $\bar{M}_w^{(8)} / \bar{M}_n^{(8)}$  is the last variable to reach the specification bands of the final grade). For comparison, Figs. 4.b-f) also present (in dashed line) the final evolutions when simple step changes into all feeds are applied at  $t=0$  min. Table 3 shows the total off-spec NBR produced with both strategies.



**Figure 4.** Change from BJLT grade to AJLT grade between Normal SSs. The off-spec product is accumulated between  $t_2=280$  and  $t_3=470$  min. a) Comonomers and CTA feed profiles into the first reactor. (b-f) Final evolutions of  $\bar{p}_A^{(8)}$ ,  $\bar{M}_n^{(8)}$ ,  $\bar{M}_w^{(8)}$ ,  $\bar{M}_w^{(8)} / \bar{M}_n^{(8)}$ , and  $\bar{B}_{n3}^{(8)}$ . For comparison, the results for simple step changes in all feeds at  $t=0$ , are shown in dashed trace.

The time evolutions for the inverse transition, AJLT→BJLT, are quite similar to the previously shown, and they are not presented here for reasons of space. Table 3 shows the total off-spec NBR produced with the two considered strategies. Compared with the simple step change, the proposed “bang-bang” strategy reduces the off-spec by 52% for BJLT→AJLT and by 35% for AJLT→BJLT.

**Table 3.** Total Off-Spec Rubber produced in the Changes of Grade between Normal SSs.

Transition	Off-Spec NBR (Kg)	
	BJLT→AJLT	AJLT→BJLT
“Bang-bang” strategy	13,630	20,950
Step change (at $t = 0$ )	28,520	32,060

## V. CONCLUSIONS

The Normal SS operation produces the same conversion, latex properties, and  $\bar{M}_n$  observed in the batch process, but with a deteriorated NBR quality indicated by higher values of polydispersity and branching degree. This effect is a consequence of the broader residence time distribution of the continuous process with respect to the batch.

Intermediate SS feeds of acrylonitrile allow controlling the copolymer composition along the train. Intermediate SS feeds of CTA allow reproducing the batch profiles of  $\bar{M}_w$ . Clearly, the efficiency of the proposed strategies will depend on the accuracy of the mathematical model.

In the SS improved operations (SS1 and SS2), acrylonitrile and CTA feeds were required in most of reactors. However, in industrial practice, it would be preferable to concentrate such additions in only a few reactors. Even though not shown for space reasons, such alternative was explored by numerical simulation and it produced acceptable results.

For changes of grade, a “bang-bang” policy was proposed, that reduced more than 35% the off-spec produced when simple step changes were applied. The proposed open-loop strategy is able to simultaneously control the molecular weights and the copolymer composition, and it is simple to apply in the industry.

## Acknowledgments

To CONICET, SECyT, and Universidad Nacional del Litoral for the financial support. To Petrobras Energía S.A. for providing us with the industrial data.

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## Appendix: Comonomer Feeds Required for Producing a Prespecified Copolymer Composition

For any generic reactor  $r$ , the steady-state mathematical model considers the following comonomer molar balances:

$$N_j^{(r-1)} \frac{q_T^{(r-1)}}{V_T^{(r-1)}} + \frac{F_j^{(r)}}{M_j} = N_j^{(r)} \frac{q_T^{(r)}}{V_T^{(r)}} + R_{pj}^{(r)}; \quad (j=A, B) \quad (\text{A.1})$$

$$N_{j,b}^{(r-1)} \frac{q_T^{(r-1)}}{V_T^{(r-1)}} + R_{pj}^{(r)} = N_{j,b}^{(r)} \frac{q_T^{(r)}}{V_T^{(r)}}; \quad (j=A, B) \quad (\text{A.2})$$

where  $N_j^{(r)}$  are the unreacted moles of comonomer  $j$ ;  $N_{j,b}^{(r)}$  are the bounded moles of comonomer  $j$ ;  $q_T^{(r)}$  is the outlet volume flow rate from reactor  $r$ ;  $F_j^{(r)}$  is the inlet mass flow rate for comonomer  $j$ ;  $M_j$  is the molecular weight of comonomer  $j$ ;  $R_{pj}^{(r)}$  is the total polymerization rate for the comonomer  $j$ ; and  $V_T^{(r)}$  is the volume of reactor  $r$ .

In each reactor  $r$ , the average mass fraction of A in the copolymer is defined as follows:

$$\bar{p}_A^{(r)} = \frac{N_{A,b}^{(r)} M_A}{N_{A,b}^{(r)} M_A + N_{B,b}^{(r)} M_B} \quad (\text{A.3})$$

Introducing the balance of Ecs. (A.1)-(A.2) into definition (A.3) we can obtain:

$$\left[ N_{B,b}^{(r-1)} \frac{q_T^{(r-1)}}{V_T^{(r-1)}} + N_B^{(r-1)} \frac{q_T^{(r-1)}}{V_T^{(r-1)}} - N_B^{(r)} \frac{q_T^{(r)}}{V_T^{(r)}} + \frac{F_B^{(r)}}{M_B} \right] \frac{p_A^{(r)} M_B}{(1-p_A^{(r)}) M_A} = N_{A,b}^{(r-1)} \frac{q_T^{(r-1)}}{V_T^{(r-1)}} + N_A^{(r-1)} \frac{q_T^{(r-1)}}{V_T^{(r-1)}} - N_A^{(r)} \frac{q_T^{(r)}}{V_T^{(r)}} + \frac{F_A^{(r)}}{M_A} \quad (\text{A.4})$$

For a prespecified value of  $\bar{p}_A^{(r)}$  ( $\bar{p}_{A,d}^{(r)}$ ), Eq. (A.4) allows estimating the feed of one of the comonomers when the other is assumed known. We propose to manipulate the feed of the more reactive comonomer (A), while the other is keep constant with the recipe and

the total feed flow. From Eq. (A.4), the following expression is derived for calculating the required  $F_A^{(r)}$ :

$$F_A^{(r)} = M_A \left\{ \left[ N_{B,b}^{(r-1)} \frac{q_T^{(r-1)}}{V_T^{(r-1)}} + N_B^{(r-1)} \frac{q_T^{(r-1)}}{V_T^{(r-1)}} - N_B^{(r)} \frac{q_T^{(r)}}{V_T^{(r)}} + \frac{F_B^{(r)}}{M_B} \right] \cdot \frac{p_{A,d}^{(r)} M_B}{(1-p_{A,d}^{(r)}) M_A} - N_{A,b}^{(r-1)} \frac{q_T^{(r-1)}}{V_T^{(r-1)}} - N_A^{(r-1)} \frac{q_T^{(r-1)}}{V_T^{(r-1)}} + N_A^{(r)} \frac{q_T^{(r)}}{V_T^{(r)}} \right\} \quad (\text{A.5})$$

where  $\bar{p}_{A,d}^{(r)}$  is the desired composition profile.

In Eq. (A.5), note that  $F_A^{(r)}$  depends on  $q_T^{(r)}$  and  $N_j^{(r)}$ , which in turn also depend on A and B feeds.

Then, for producing the desired profile  $\bar{p}_{A,d}^{(r)}$ , we proposed to keep  $F_B^{(1)}$  at its Normal SS value, while all the other B feeds are zero, and apply the following iterative procedure for calculating  $F_A^{(r)}$ :

- i) for  $q_T^{(r)}$  and  $N_j^{(r)}$ , adopt the Normal SS operation values;
- ii) estimate  $F_A^{(r)}$  from Eq. (A.5) and solve the polymerization model;
- iii) compare the values of  $q_T^{(r)}$ ,  $N_j^{(r)}$  and  $\bar{p}_A^{(r)}$  with their previous values, and repeat from ii) until convergence.