

An Optimized Mixing Approach for Improved Anode Quality

Fabien Gaudière¹, Christophe Bouché², Salima Belbachir³ and Quentin Bernabé⁴

1. Innovation Manager

2. Product & Innovation Director

3. Process Engineer

Fives Solios, Givors, France

4. PhD Student

Université de Haute Alsace – CNRS IS2M UMR 7361, Mulhouse, France

Corresponding author: fabien.gaudiere@fivesgroup.com

<https://doi.org/10.71659/icsoba2025-el009>

Abstract

In recent years, anode property optimization has mainly been obtained through dry mix, mixing or forming process improvements. Another way to enhance anode properties is to work on raw materials and to study the ability of coal tar pitch to coat and penetrate coke porosities. This paper describes a new approach for paste mixing in two steps to improve anode quality: (i) blending a low viscosity coal tar pitch (CTP) with the grain fraction of the calcined petroleum coke (CPC) recipe to maximize filling of open porosities, (ii) incorporating a high viscosity CTP and the fine fraction of the dry mix into the previously obtained blend. The two sequences are performed at two different temperatures ($T_{\text{step 1}} < T_{\text{step 2}}$). The major goal of this two-steps mixing is to maximize the filling of open coke porosities, therefore, to enhance anode quality. The resulting paste is then used to form lab-scaled anodes, which are baked and characterized. Their quality can be quantified by calculating the net carbon consumption, on the basis of a widely acknowledged formula. The results show an improvement of lab-scaled anode quality produced following this sequenced-mixing process, along with a significant decrease of the calculated net carbon consumption.

Keywords: Anode, Calcined petroleum coke, Coal tar pitch.

1. Introduction

The performance of carbon anodes in Hall-Héroult electrolysis remains a major factor in aluminium production efficiency. Over the past decades, industrial innovations have successively improved key production steps from aggregate preparation to mixing and compaction. For example, the introduction of the Rhodax® crusher [1] with its inertial compression mechanism enables selective fragmentation, preserving coarse particles while breaking down porous ones, thus producing a dry aggregate with a high Grain-to-Sand (G/S) ratio. This optimized granular skeleton contributes to better compaction, thermal shock resistance, and anode integrity [2].

Subsequent advances included the implementation of vacuum-assisted vibrocompaction, improving paste densification and structural uniformity. More recently, attention has shifted to the mixing stage with the deployment of the IMC (Intensive Mixing Cascade) [3]. This technology allows fine control over temperature, timing, and pitch addition, making it possible to precisely manage the interaction between pitch and aggregate.

Despite these innovations, conventional mixing protocols still require a single pitch to simultaneously infiltrate coke porosity and coat particle surfaces two functions difficult to optimize under uniform conditions. This often leads to incomplete pore filling and heterogeneous coating. Previous studies, including sessile drop experiments conducted by Bernabé *et al.*, have shown that pitch penetration efficiency depends not only on temperature and porosity, but also on

the pitch viscosity and chemical affinity with the coke surface [4]. These findings underscore the need for tailored rheological properties and appropriate mixing sequences to optimize pitch distribution and utilization at the grain level. The wettability of coke by pitch is of primary importance for aluminium producers and is the subject of ongoing scientific research [5, 6].

Beyond process efficiency, improving pitch distribution may also contribute to reducing polycyclic aromatic hydrocarbon (PAH) emissions, with positive implications for environmental impact and occupational health. The use of high-viscosity pitches rich in high molecular weight PAHs and lower in volatile fractions combined with a better balance between impregnation and binder functions, may further help limit the release of volatiles during baking.

To overcome these limitations, this study investigates a sequenced mixing protocol using two coal tar pitch grades with contrasting viscosities. A low-viscosity pitch is first applied to the coarse fraction to promote pitch penetration, followed by a high-viscosity pitch added with fines to enhance surface coating and final cohesion. The approach leverages the thermal flexibility of IMC equipment and aims to decouple the roles of impregnation and coating. This process has been patented [7].

Through laboratory trials, this paper compares conventional and sequenced protocols across multiple pitch contents and distributions. Results are interpreted through key performance indicators density, electrical resistivity, reactivity, and net carbon consumption (NCC) with additional insight into the energy balance during baking.

2. Experimental Works

2.1 Raw Materials

2.1.1 Calcined Petroleum Coke and Butts

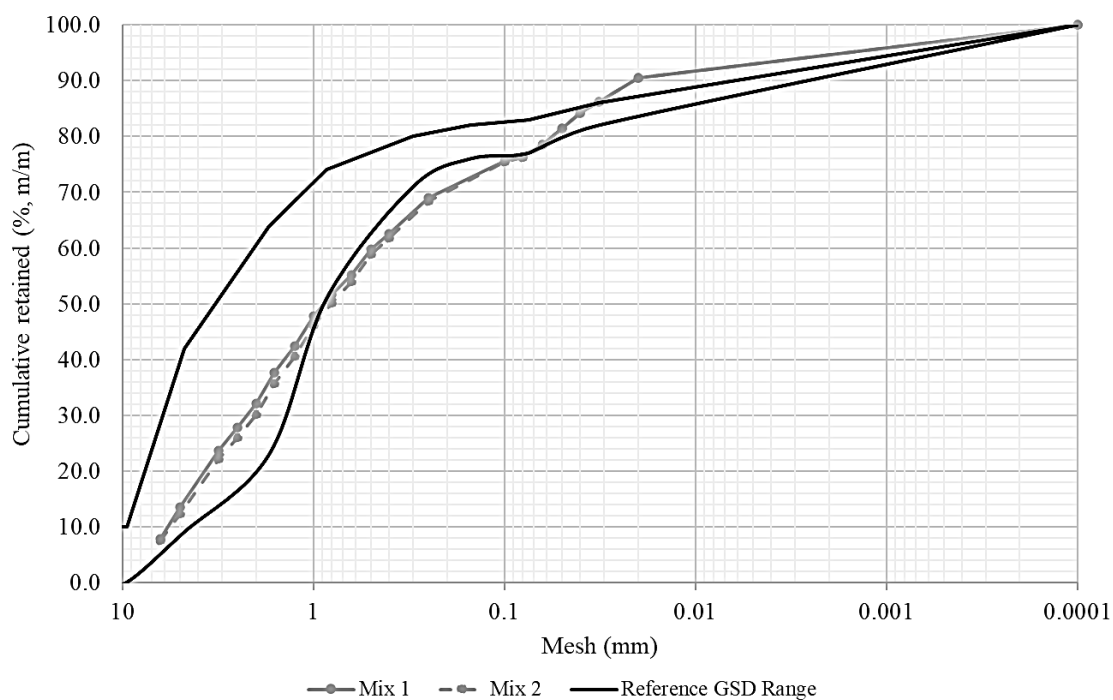


Figure 1. Grain size distribution (GSD) of the CPC aggregate used for laboratory anodes, compared to the SCAP-Rhodax® process reference range (in cumulative retained).

Calcined petroleum coke (CPC) and butts (Table 1) were supplied by Aluminium Dunkerque. The CPC was sieved into four granular fractions: 8–4.7 mm, 4.7–1.7 mm, 1.7–0.15 mm, and < 0.15 mm (fines). The butts were crushed and blended to simulate industrial recycled content. The dry raw material preparation, including crushing and sieving, was carried out at the Fives FCB pilot testing centre. The blend proportions used were: 25 % for TG (8–4.7 mm), 20 % for G (4.7–1.7 mm), 33 % for M (1.7–0.15 mm), and 22 % for fines (<0.15 mm), resulting in a 5.5 kg batch (Figure 1). In the following sections, the coarse fraction refers to the combined TG, G, and M classes (i.e., particles >150 μm), while the fine fraction corresponds to particles smaller than 150 μm .

Table 1. Summary of CPC and butts properties used for laboratory anodes fabrication.

Property		Method	Value	
			CPC	Butts
Tapped bulk density (kg/dm^3)	8-4 mm	ISO 10236	0.69	0.92
	4-2 mm		0.76	0.92
	2-1 mm		0.83	0.93
	1-0.5 mm		0.92	0.93
	0.5-0.25 mm		0.94	0.93
Real density kg/dm^3		ISO 8004	2.059	2.103
Ash (wt %)		ISO 8005	0.18	0.98
XRF analysis	S (%)	ISO 12980	2.02	1.49
	V (ppm)		246	213
	Ni (ppm)		157	129
	Si (ppm)		82	74
	Fe (ppm)		101	496
	Na (ppm)		41	984
	Ca (ppm)		108	245
Hg porosimetry	Apparent density (100 μm) kg/dm^3	DIN 66133	1.66	1.70
	Apparent density (13 μm) kg/dm^3		1.79	1.77
	Accessible porosity %		17.8	16.6

2.1.2 Controlled Softening Point Pitches

CTP was also supplied by Aluminium Dunkerque. A standard softening point pitch (SSP) was used as the base material. Two derivatives were produced:

- **LSP (Low Softening Point Pitch)**: obtained by fluxing SSP with light oils recovered during vacuum distillation.
- **HSP (High Softening Point Pitch)**: obtained by vacuum distillation of SSP up to ~ 420 °C under reduced pressure.

Target softening points were 80–85 °C for LSP and ~ 150 °C for HSP (Mettler method). To adjust the softening point, a rule of thumb was applied: 3 °C shift per 1 % oil added/removed.

The vacuum distillation and fluxing protocols used to tailor the softening point of the pitches were developed in collaboration with Fives ProABD, whose technical expertise supported the selection of temperature conditions and the balance of light and heavy fractions. This partnership ensured both consistency and scalability of the pitch modification process for laboratory and industrial purposes.

2.1.3 Vacuum distillation

To perform vacuum distillation, standard CTP was poured into a flask and heated up to 300 °C (Figure.2). Vacuum was then made in the distillation assembly and very carefully increased to avoid extracting heavy oils into the cooling column. Temperature of liquid pitch in the flask and

vapours in the Vigreux column were monitored, as well as the vacuum pressure. The light oils are collected in the distillate.

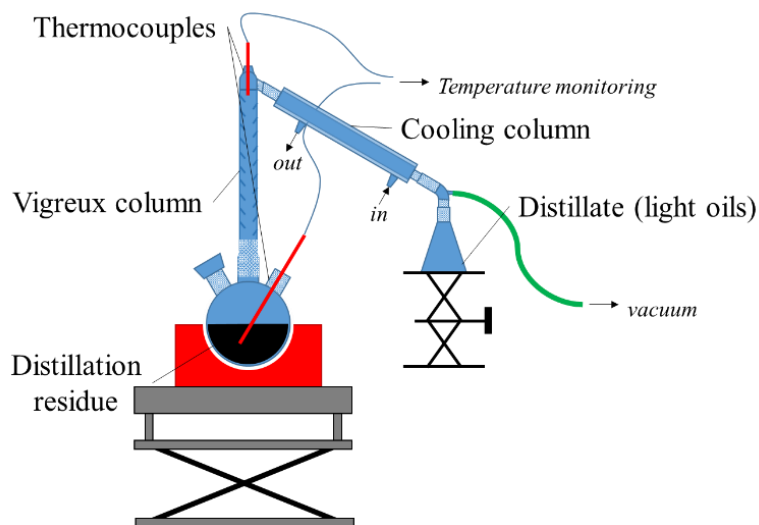


Figure 2. Schematic of the vacuum distillation assembly used to modify the softening point of coal tar pitch through selective removal of light fractions.

A maximum temperature of 420 °C was accepted at the end of the process, in order to avoid reforming phenomena, which could have led to formation of heavy PAH or mesophases in the liquid pitch (Figure 3).

In order to estimate the amount of light oils to distillate, a ratio of 3 °C / %_{oil} was used. Thus, as the amount of SSP at the beginning of each distillation was 2.5 kg, and the difference between the softening points of HSP and SSP was 33.8 °C, the amount of light oils at the end was around 280 g.

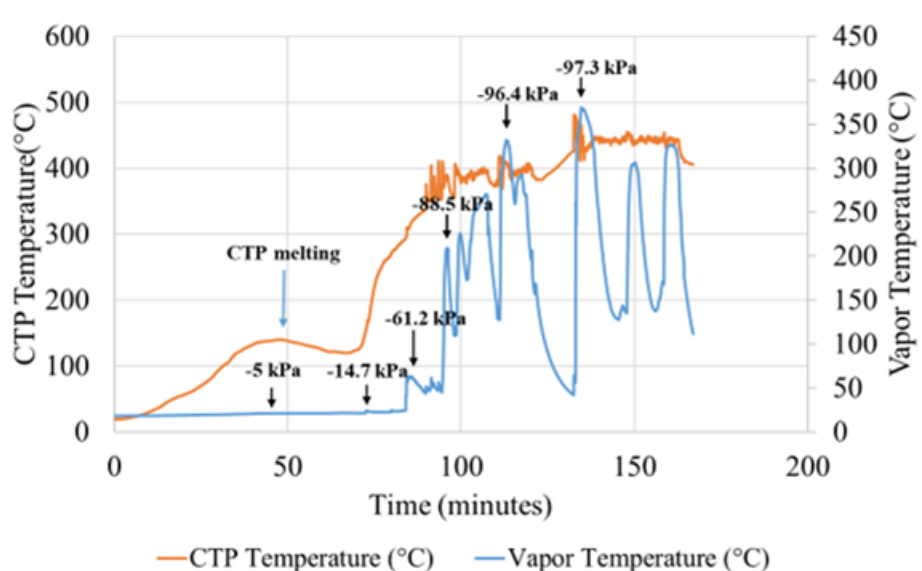


Figure 3. Temperature profile during vacuum distillation of coal tar pitch (CTP). The CTP temperature (orange curve) and vapor phase temperature (blue curve) are plotted against time, along with corresponding pressure setpoints.

2.1.4 Fluxing

LSP was obtained by fluxing of standard CTP with light oils obtained during the vacuum distillation process. SSP was slowly heated to 130 °C with a given amount of oils, in a flask equipped with a Vigreux column, until the formation of a homogenous blend (Figure 4). The temperature of the blend was monitored in order to avoid overheating.

To calculate the amount of light oils to add to SSP, the same rule of 3 °C / %_{oil} was used. As an example, for a batch of 2000 g of LSP, around 250 g of light oils were poured into the flask with the CTP.

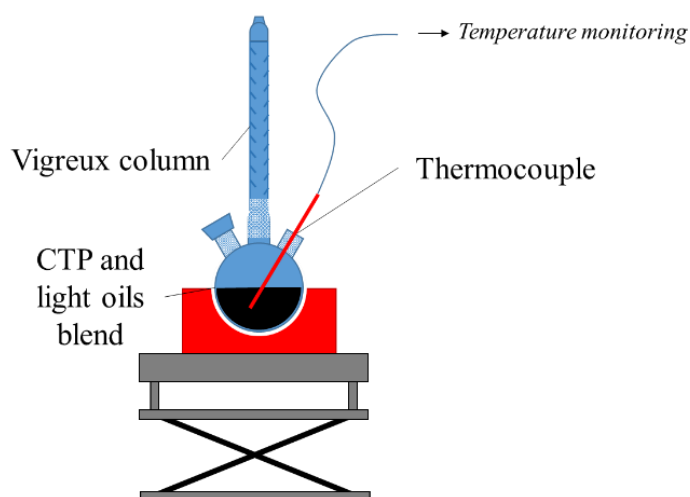


Figure 4. Schematic of the laboratory setup used to adjust the softening point of coal tar pitch by controlled addition of light aromatic fractions (fluxing).

2.1.5 Coal Tar Pitches Characterization

Coal tar pitches (CTPs) used in this study were characterized at the Fives ProABD laboratory using standardized methods (Table 2).

Table 2. Summary of pitch properties for LSP, SSP, and HSP grades: softening point, toluene and quinoline insoluble, β -resin content, coking value, and dynamic viscosity at 186 °C.

Property	Method	Value		
		LSP	SSP	HSP
Softening Point (°C)	D3104	84.7	116.2	154.3
Toluene-insoluble (wt %)	D4402-87	20.4	24.1	36.0
Quinoline-insoluble (wt %)	D4072	6.7	6.9	10.4
β resin (w t%)	D2318	13.5	17.2	25.6
Coking Value (% _m)	D2416-84	49.0%	57.0%	69.7%
ν (186°C) (mPa/s)		36.98	489.28	20566.13

The viscosity measurements confirmed that CTP behaves as a Newtonian fluid in the temperature range relevant to anode paste preparation. As expected, the viscosity of each pitch grade decreased exponentially with increasing temperature, as shown in Figure 5. Furthermore, a strong correlation was observed between softening point and viscosity at a given temperature: the higher the softening point, the greater the viscosity. This trend is consistent with the increase in molecular weight and aromatic complexity of the heavier pitch fractions.

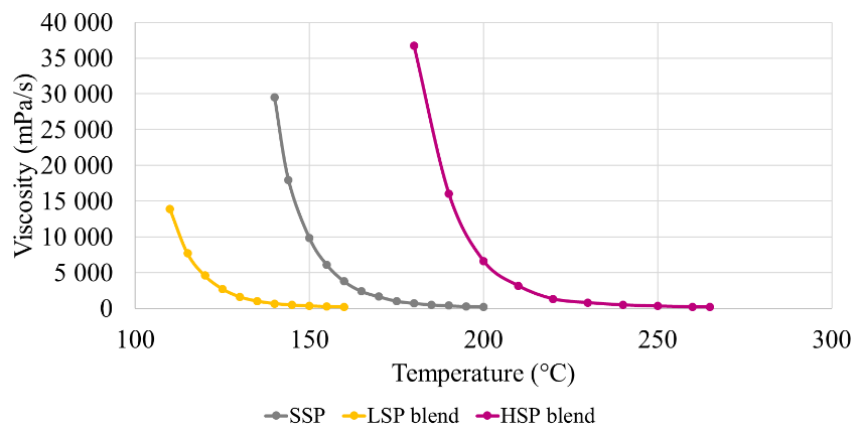


Figure 5. Viscosity profiles of standard soft pitch (SSP), low-softening-point pitch (LSP), and high-softening-point pitch (HSP) as a function of temperature.

2.2 Preparation of Laboratory-Scale Anodes

All laboratory-scaled anodes were produced in the Fives Solios's laboratory facility, in Mulhouse, France, using the same dry recipe composed of CPC and recycled butts. The granular fraction (TG, G and M) and fines were proportioned as described previously, to form 5.5 kg batches. The dry blend was preheated to the target temperatures prior to pitch addition according to a specific mixing protocol.

2.2.1 Mixing Protocols

The anodes were prepared using two main mixing methods:

- **One-step mixing (M1):** All coke fractions were combined, preheated for 12 hours at 200 °C, and then mixed with solid pitch at 186 °C for 11 minutes. This method served as the reference process.
- **Sequenced mixing (M2 and M3):** The coarse and fine fractions were preheated separately. First, the coarse fraction was mixed with the initial pitch portion at 186 °C for 6 minutes. Then, the mixer was paused to add the second pitch portion and the preheated fines, followed by another 6-minute mixing step. In protocol M2, this second mixing step was performed at 186 °C using SSP pitch, whereas in protocol M3, it was carried out at 240 °C using HSP pitch.

2.2.2 Anode Forming and Baking

The mixing operations were carried out using a high-temperature Eirich RV02E mixer. Depending on the chosen process (M1, M2, or M3), both the mixing sequence and temperatures were adjusted accordingly. The pitch content and its distribution were also varied as follows:

- Pitch content:
 - 14 % → 0.895 kg
 - 16 % → 1.050 kg
 - 18 % → 1.210 kg
- Pitch distribution (mass applied to the coarse fraction):
 - P30 → 0.315 kg
 - P50 → 0.525 kg

The amount of pitch added during the second mixing stage was determined by subtracting the mass added in the first stage from the total pitch content. For instance, in a protocol using 18 %

CTP with a P30 distribution, 0.315 kg is added in the first stage and the remaining 0.895 kg (i.e., 1.210 kg – 0.315 kg) is incorporated during the second stage.

Immediately after mixing, the hot paste was transferred into cylindrical moulds (100 mm diameter), without cooling step, and pressed using a Shimadzu AGSX 100 kN press up to a final compaction pressure of 11.5 MPa. For each batch, three anodes of 2 kg were formed. A temperature probe was inserted 5 cm into the center of each green anode to ensure consistency in paste temperature immediately after forming. Measurements taken at this stage indicated temperatures of approximately 160–170 °C when mixing occurred at 186 °C, and 220–230 °C when mixing was done at 240 °C. These readings served solely as indicators of protocol repeatability and were not considered analytical variables.

After weighing and dimensional measurements, two green anodes of each batch were shipped to R&D Carbon Ltd for baking and analysis. These anodes were baked under controlled conditions and fully characterized. The third was preserved for microscopy and potential image analysis.

2.2.3 NCC Calculation

Among the properties measured for the estimation of the quality of the laboratory-scale anodes, four of them were used to calculate the NCC of the anodes, as expressed in the following equation, as described by Fischer et al. [8]:

$$\text{NCC} = C + \frac{334}{\text{CE}} + 1.2 \times (\text{BT} - 960) - 1.7 \times \text{CRR} + 9.3 \times \text{AP} + 8 \times \text{TC} - 1.5 \times \text{ARR} \quad (1)$$

where:

C	Carbon coefficient, kg C/t Al, typically between 270 and 310
CE	Current efficiency, typically 0.82–0.95
BT	Bath Temperature, °C, typically between 945 and 980
ARR	Air Reactivity Residue, wt. %
CRR	CO ₂ Reactivity Residue, wt. %
AP	Air Permeability, nPm
TC	Thermal Conductivity, W/m·K

The Air Reactivity Residue (ARR) and CO₂ Reactivity Residue (CRR) were determined using thermogravimetric analysis (TGA, ASTM C1171). This method involves subjecting baked anode samples to controlled oxidizing atmospheres (air or CO₂) and measuring the residual mass after exposure. The lower the residue, the higher the reactivity of the anode to gas attack. These tests were aligned with ASTM C1171 and further refined through internal protocols developed in collaboration with R&D Carbon Ltd.

Air permeability (AP) was measured using a setup compliant with DIN 66133. This test evaluates the ease with which gases can diffuse through the anode microstructure. It is a critical indicator of the compactness and structural integrity of the anode. Lower permeability values indicate a denser, less porous structure, which is generally associated with better performance and lower reactivity.

Thermal conductivity (TC) was assessed using Laser Flash Analysis (LFA), a technique that measures the material response to a thermal pulse. This property is essential for evaluating the ability of the anode to dissipate heat during electrolysis. Higher thermal conductivity contributes to better thermal management and reduced thermal gradients within the cell.

These parameters were benchmarked against industrial cell conditions to simulate real-world performance. The formula allows for a predictive and comparative assessment of anode quality, highlighting the influence of both material properties and process parameters.

2.2.4 Design of Experiments and Anodes Nomenclature

To fully assess the influence of these modified pitches and their distribution during mixing, a complete Design of Experiments (DoE) was established. This experimental plan encompassed variations in pitch content (14 %, 16 %, and 18 %), pitch types (SSP, HSP, and LSP), and repartition ratios between the two mixing sequences (P30 and P50). The protocols tested M1 (one-step), M2 (sequenced with single pitch), and M3 (sequenced with dual pitch) were selected to evaluate the interaction between binder distribution, temperature, and rheology. This matrix approach enabled a robust comparative analysis across all critical anode properties, and was instrumental in identifying the optimal formulation parameters for enhanced carbon efficiency and structural integrity.

In the following sections, anode batches are identified using a standardized nomenclature based on four parameters: **Mixing Protocol – Pitch Type – Pitch Content – Pitch Distribution**. For example, an anode produced with a sequenced mixing protocol using standard soft pitch only (M2 SSP), with 16 % CTP and a 50/50 distribution between the two mixing stages, will be referred to as M2 SSP 16 P50.

3. Results

3.1 Influence of Pitch Content in Standard Mixing

Initial trials focused on the influence of pitch content in the standard one-step mixing protocol (M1), using three levels of CTP: 14 %, 16 %, and 18 %. The objective was to identify an optimal formulation that balances structural integrity, electrical performance, and processability.

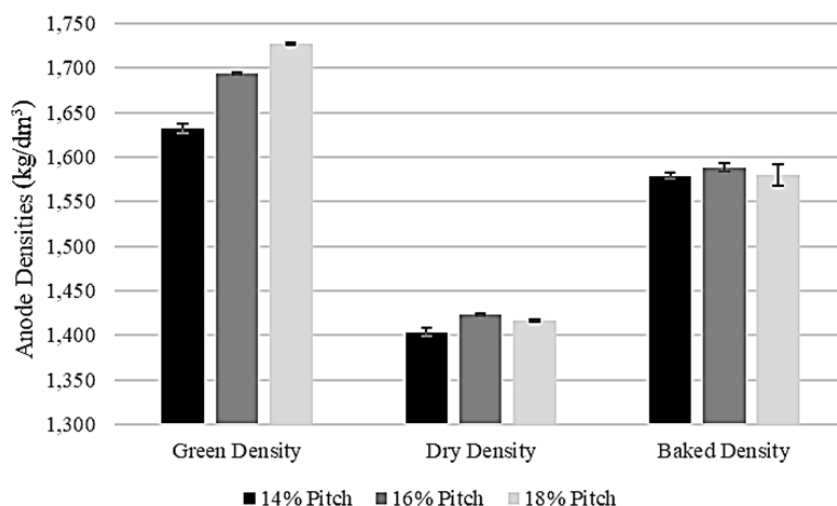


Figure 6. Green, dry, and baked anode densities as a function of pitch content (14 %, 16 %, and 18 % - in black, dark gray and light gray respectively).

Green and dry densities (Figure 6) both increased when pitch content was raised from 14 % to 16 %, indicating improved compaction and better binder dispersion within the dry carbon framework. Green density rose from 1.632 to 1.694 kg/dm³, while dry density peaked at 1.423 kg/dm³ for 16 %, before slightly decreasing to 1.416 kg/dm³ at 18 %. This decline in dry

density suggests that, beyond 16 % pitch content, the additional binder no longer contributes effectively to skeletal packing, possibly due to saturation. Baked density followed a similar trend, increasing to 1.589 kg/dm³ at 16 % before falling back to 1.580 kg/dm³ at 18 %. These observations confirm that 16 % CTP provides the best compromise between binder content and structural integrity for this aggregate, while 18 % results in over-saturation, internal void formation, and reduced dimensional stability during baking.

Table 3. Key parameters of M1 anodes for 14 %, 16 % and 18 % total SSP content

Protocol	Sticking of Packing Coke (% m/m)	Backing Loss (%)	Electrical Resistivity ($\mu\Omega\cdot\text{m}$)
M1 SSP 14	0.18 \pm 0.08	4.88 \pm 0.08	61.0 \pm 1.4
M1 SSP 16	2.45 \pm 0.25	5.58 \pm 0.08	55.6 \pm 0.4
M1 SSP 18	4.38 \pm 0.16	6.48 \pm 0.01	60.0 \pm 3.7

A similar pattern was observed in electrical resistivity, which reached its lowest value at 16 % CTP (55.6 $\mu\Omega\cdot\text{m}$), compared to 61.0 and 60.0 $\mu\Omega\cdot\text{m}$ at 14 % and 18 %, respectively. These results suggest that 16 % of CTP offers the best balance between binder quantity and carbon bonds (Table 3).

Other parameters also deteriorated at higher pitch contents. Baking loss increased steadily from 4.88 % at 14 % to 6.48 % at 18 %, reflecting higher volatile evolution during baking, that could lead to internal cracks or degassing pathways within the anode. Additionally, sticking to the packing coke used as an indicator of paste stickiness and surface over-wetting increased markedly from 0.18 at 14 % to 4.38 at 18 %, suggesting increased handling difficulties.

Based on these results, the 16 % pitch content was selected as the standard for subsequent comparative trials using sequenced protocols. It provided the best compromise between structural cohesion, electrical performance, and operational viability.

3.2 Comparative Performance of One-stepped and Sequenced Mixing Protocols

This section compares the performance of the standard M1 protocol (single-step mixing at 16 %) with two sequenced alternatives: M2, using a single pitch (SSP), and M3, using a dual-pitch combination (LSP + HSP). All protocols were tested at 14 % and 16 % pitch content, with pitch distributions of P50 and P30 as described in the Experimental Works section. Performance was evaluated based on green and baked density, AP, reactivity to CO₂ and air (CRR, ARR), electrical resistivity, and net carbon consumption (NCC).

In the M1–M2 comparison (Figure 7, top row), green and baked densities remained comparable across both protocols. For example, M2–16 % with P50 pitch distribution reached 1.691 kg/dm³ (GAD) and 1.594 kg/dm³ (BAD), close to M1's values. Notably, AP decreased significantly in M2, dropping to 1.05 nPm at 14 % CTP compared to 2.62 nPm in M1 at 16 % (Table 4). Electrical resistivity remained stable at 55.8 $\mu\Omega\cdot\text{m}$ (M2–16 %) versus 55.6 $\mu\Omega\cdot\text{m}$ (M1), while reactivity values showed marginal improvements or similar performance. NCC was particularly revealing: M1–16 % exhibited 424 kg C/t Al, while M2–14 % (P30) reached as low as 410 kg C/t Al. These results confirm that even with a single pitch, sequencing improves binder distribution and allows for lower pitch content without compromising structural integrity or carbon efficiency.

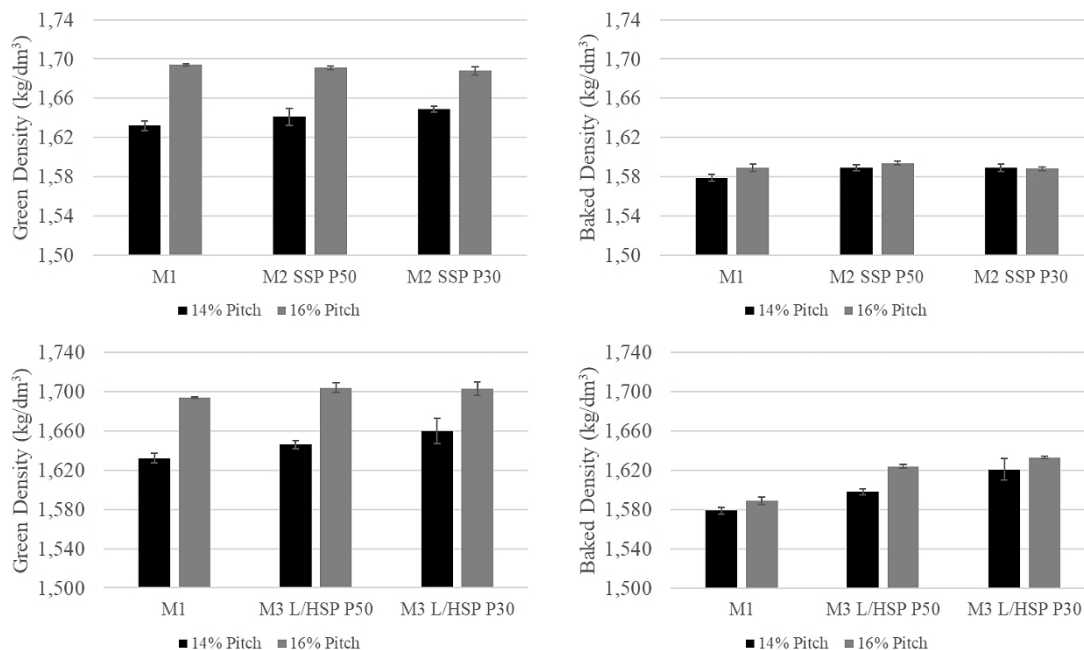


Figure 7. Green (left column) and baked (right column) densities of anodes produced with M1 and M2 protocols (top row) and M1 and M3 protocols (bottom row) at 14 % and 16 % pitch content (in black and dark gray respectively).

Table 4. Comparison of key properties (Electrical Resistivity, AP and NCC) between M1, M2 and M3 protocols for 14 % and 16 % total CTP content and P30 and P50 distribution

Protocol	Electrical Resistivity ($\mu\Omega\cdot\text{m}$)	Air Permeability (nPm)	NCC (kg C/t Al)
M1 SPP 14	61.0 ± 1.4	2.18 ± 0.54	424
M1 SSP 16	55.6 ± 0.4	2.62 ± 0.10	424
M2 SSP 14 P50	59.8 ± 4.4	1.05 ± 0.08	414
M2 SSP 16 P50	55.8 ± 0.5	1.49 ± 0.09	412
M2 SSP 14 P30	59.0 ± 1.6	1.04 ± 0.32	410
M2 SSP 16 P30	57.5 ± 3.3	1.57 ± 0.03	417
M3 L/HSP 14 P50	70.4 ± 1.8	1.69 ± 0.23	418
M3 L/HSP 16 P50	54.3 ± 0.5	1.12 ± 0.05	405
M3 L/HSP 14 P30	60.0 ± 3.2	1.14 ± 0.15	427
M3 L/HSP 16 P30	59.0 ± 0.1	1.05 ± 0.01	404

M3 introduced further enhancements by combining a low-viscosity pitch (LSP) for pore infiltration and a high-viscosity pitch (HSP) for coating. At 16 %, M3–P30 yielded the highest green and baked densities observed (Figure 7, bottom row), reaching 1.703 and 1.633 kg/dm³, respectively, while AP dropped to 1.05 nPm. Electrical resistivity also improved, with a value of 53.4 $\mu\Omega\cdot\text{m}$ compared to 55.6 $\mu\Omega\cdot\text{m}$ in M1. NCC decreased to a minimum of 403–405 kg C/t Al, representing a 20 kg C/t Al improvement over M1. These gains highlight the effectiveness of decoupling pitch functions across mixing stages. However, at 14 % CTP with a P30 distribution, M3 exhibited signs of instability: AP increased and NCC rose to 448.8 kg C/t Al. Results are summarized in Table 4. This outcome suggests that the total pitch content was insufficient to ensure proper impregnation of the coarse fraction in the first stage, and simultaneously too limited to form a cohesive matrix during the second. As a result, the anode structure remained under-

bound and more permeable, highlighting the limitations of underdosage when combined with an unbalanced pitch repartition.

A direct comparison at 16 % CTP between the three protocols confirmed the trend: NCC values dropped from 424.3 kg C/t Al (M1) to 411.8 kg C/t Al (M2–P50), and further to 403.6 kg C/t Al (M3–P30). Baked density followed the same trend, increasing from 1.570 kg/dm³ (M1) to 1.582 (M2) and 1.588 kg/dm³ (M3). AP decreased steadily from 2.62 nPm in M1 to 1.05 nPm in M3. The gains in M3 were consistent across multiple indicators, confirming its effectiveness when pitch type, distribution, and sequence timing are all optimized.

Overall, the results confirm that pitch sequencing significantly enhances anode performance compared to standard one-step mixing. M2 demonstrates that sequencing alone, even with a single pitch, brings structural and reactive benefits. M3 builds on this by tailoring pitch viscosity to each mixing stage, yielding the best overall performance at 16 % pitch content. These improvements, however, are contingent upon maintaining optimal pitch ratios and total content, as over- or under-pitching can negate the expected benefits.

However, this enhanced performance relies not only on the protocol itself but also on maintaining optimal pitch content. The effect of increased pitch will be addressed in the next section.

For the following experiments, we choose to focus on P50 CTP distribution, in order to maximize the quantity of pitch that could penetrate the CPC open porosities.

3.3 Influence of Pitch Type and Content

To further investigate the role of pitch quantity and rheology, additional anode series were fabricated using a high-softening-point pitch (HSP) and increasing the total pitch content from 16 % to 18 %. These trials were carried out across three mixing protocols:

- M1: standard one-step mixing with HSP
- M2: sequenced mixing with HSP (both sequences)
- M3: sequenced dual-pitch mixing (SSP in step 1, HSP in step 2)

For all the protocols, the mixing temperature was raised to 240 °C, consistent with the high viscosity of HSP. At 240 °C, the viscosity of HSP exhibit a viscosity of 488 cP, while SSP pitch show a viscosity of 489 cP at 186 °C.

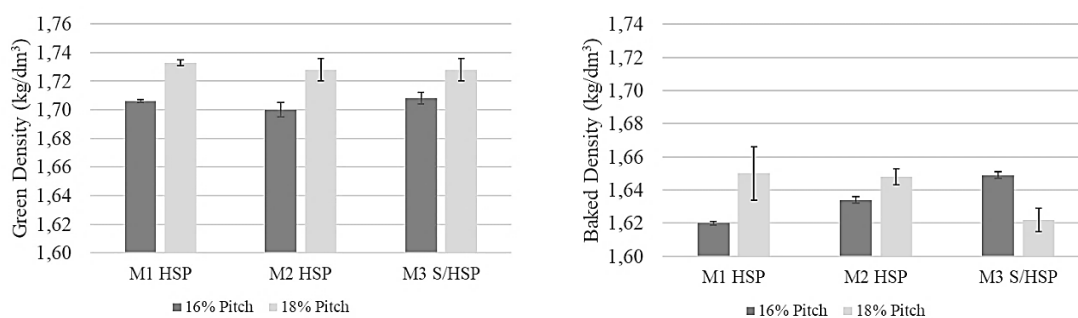


Figure 8. Green (left) and baked (right) densities of anodes produced with M1, M2 and M3 protocols at 16 % and 18 % pitch content (in dark and light gray respectively).

The experimental results clearly demonstrate that increasing pitch content beyond 16 % leads to measurable structural and reactive degradation in all mixing protocols tested. While an increase in pitch from 14 % to 16 % tends to improve green and baked densities (Figure 8), this benefit quickly plateaus and may even reverse at higher levels, particularly in sequenced protocols such

as M3. For instance, although the baked density of M3 anodes decreases when CTP ratio increases from 16 % to 18 % (from 1.649 to 1.622 kg/dm³), this loss is accompanied by a dramatic rise in AP (from 0.85 to 4.65 nPm), pointing to the formation of internal porosities or microcracks during the baking process. A similar pattern is observed in M1 and M2, confirming that the system becomes structurally unstable when excess binder is present.

Table 5. Comparison of key properties (Electrical Resistivity, AP and NCC) between M1, M2 and M3 protocols for 16 % and 18 % total CTP with P50 distribution.

Protocol	Electrical Resistivity (μΩ.m)	Air Permeability (nPm)	NCC (kg C/t Al)
M1 HSP 16	50.6 ± n/a	1.35 ± n/a	413
M1 HSP 18	52.4 ± 1.6	4.35 ± 0.40	441
M2 HSP 16	52.6 ± n/a	1.21 ± n/a	401
M2 HSP 18	51.0 ± 0.9	3.36 ± 0.62	420
M3 S/HSP 16	52.1 ± n/a	0.85 ± n/a	401
M3 S/HSP 18	53.4 ± 0.4	4.65 ± 1.45	437

In terms of NCC, all protocols exhibit higher values at 18 % CTP. M3, for example, sees the NCC increase from 401 to 437 kg C/t Al, essentially erasing the performance gains obtained through optimized pitch sequencing. M1 also experiences a rise from 413 to 441 kg C/t Al, while M2 increases from 401 to 420 kg C/t Al. These shifts correlate with increased reactivity: both ARR and CRR values are higher in most 18 % trials, which suggests a broader exposure of reactive surfaces. This behaviour is likely due to the accumulation of volatiles during baking. At high pitch contents, the release of volatiles can lead to the formation of preferential degassing pathways, which in turn generate open porosity within the anode structure. Results are summarized in Table 5.

The data further confirm that simply increasing the pitch content does not ensure better performance, even when applying high mixing temperatures (240 °C) with HSP. On the contrary, this strategy introduces structural risks that compromise the anode’s integrity, leading to higher porosity, elevated electrical resistivity, and greater carbon loss.

Overall, the findings emphasize the importance of precise binder formulation. Maintaining a pitch content of 16 % appears to offer the best balance between structural integrity and carbon efficiency for the specific aggregate used for this study. Above this threshold, the negative effects of over-saturation outweigh any marginal gains in density, even within a carefully optimized mixing process.

3.4 Baking Loss and Energy Balance

In addition to structural and reactive properties, the anodes were evaluated based on their contribution to the baking furnace energy balance. This contribution stems from volatile matter released during pitch pyrolysis, including light hydrocarbons, methane (CH₄), and hydrogen (H₂), which combust and provide in-situ thermal energy during the firing cycle.

Table 6. Baking loss (% mass loss) for different mixing protocols at 16 % pitch content.

Property	M1 SSP 16	M1 HSP 16	M2 HSP P50 16	M3 S/HSP P50 16
Baking Loss (% m/m)	5.6	4.2	4.3	4.6

The baking loss was calculated by measuring the mass difference between green and baked anodes (Table 6). This loss represents the degassed fraction, primarily from pitch decomposition. The baking loss serves as a proxy to estimate the internal energy yield of the anode.

- For the reference M1 (16% SSP), the baking loss yielded an energy contribution of approximately 1.90 GJ/t.
- In contrast, anodes made with HSP-based M3 (16%) showed reduced volatile content and a lower degassing profile, resulting in only 1.57 GJ/t of internal energy a reduction of ~17%.

The decrease in internal energy contribution must be offset by additional fuel injection (natural gas or fuel oil) to maintain the required temperature profile inside the baking furnace and prevent under-baking or structural cracking.

An energy balance based on the net calorific value (NCV) of gases emitted by pitch was used to estimate this need:

- NCV values:
 - Volatiles: 40.75 MJ/kg
 - CH₄: 50.02 MJ/kg
 - H₂: 119.93 MJ/kg
- Standard gas distribution: Volatiles 82 %, CH₄ 11 %, H₂ 7 %
- Natural gas NCV: ≈ 36.5 MJ/Nm³

From this, the energy shortfall of 0.33 GJ/t (1.90–1.57 GJ/t) for M3 (16 %) was calculated to require ~ 9 Nm³/t of additional natural gas injected into the baking furnace.

While this compensation represents an economic and operational cost, it must be balanced against the benefits of reduced PAH emissions, improved structural quality, and lower net carbon consumption. It also emphasizes the need to adapt baking curves when using high-softening-point pitches: extending holding times, adjusting ramp rates, or optimizing fuel injection strategies.

4. Discussion

4.1 Mechanisms Behind the Improved Performance

The improvements observed with sequenced mixing protocols particularly M3 stem from the deliberate separation of two essential binder functions: pore infiltration and surface coating. In the first stage, a low-viscosity pitch (LSP) is mixed with the coarse coke fraction at 186 °C. This promotes capillary penetration into the open porosity of the larger grains, enabled by the pitch's lower viscosity, higher fluidity, and enhanced wettability.

The second stage, carried out at 240 °C, involves the addition of a high-viscosity pitch (HSP) together with fines. This step reinforces the binder network through surface coating, contributing to higher carbon yield thanks to HSP's elevated β -resin content and coking value. This two-step approach ensures that each pitch fraction operates under optimized conditions: LSP serves its role in pore filling, while HSP consolidates the structure.

This strategy contrasts with the conventional one-step mixing (M1), where a single pitch must fulfil both roles simultaneously, often under suboptimal conditions. As a result, one-step processes can lead to heterogeneous pitch distribution, inefficient infiltration, and uneven coating, especially with high-viscosity binders.

These experimental findings align with previous theoretical and laboratory work on pitch/coke interaction [9]. Sessile drop penetration tests and capillary flow modelling have shown that impregnation depends not only on viscosity but also on the molecular affinity between pitch and

coke surfaces [10]. Such insights help rationalize the benefits of using a softer pitch in the early stage, followed by a stiffer pitch for mechanical reinforcement.

Moreover, the molecular interactions between polycyclic aromatic hydrocarbons (PAHs) in the pitch and the graphitic layers of the coke surface play a significant role. Studies have demonstrated that π - π stacking interactions between these aromatic systems can enhance the adhesion and spreading of the pitch on the coke surface, facilitating better impregnation and coating. This molecular affinity contributes to the improved structural integrity and performance of the anodes produced using sequenced mixing protocols [11].

Altogether, the results confirm that sequenced mixing, especially when tailored through pitch rheology and controlled thermal input, provides a robust path toward reducing porosity, improving structural uniformity, and lowering net carbon consumption. Moreover, this approach offers a flexible platform for integrating bio-sourced additives in the future, particularly in the first sequence, to fine-tune viscosity and improve sustainability without compromising performance.

4.2 Sequenced Mixing: A Shift from Quantity to Distribution

The results clearly demonstrate that beyond pitch quality, the efficiency of binder utilization depends critically on its distribution during mixing. Increasing CTP content alone does not guarantee better performance; on the contrary, tests at 18 % CTP showed that excess pitch rather than being absorbed by the porous coke tended to saturate the matrix, creating internal pressure during baking. This led to the formation of microcracks and gas escape pathways, increasing AP and carbon reactivity. These outcomes confirm that a well-distributed 16 % pitch, applied in sequence and aligned with the pore structure, outperforms higher binder contents applied in a single step, even when pitch quality is high.

At 18 % pitch, excess binder led to volatile saturation, increased baking loss, gas channelling, and lower baked density. The M3 protocol at 16 % CTP outperformed its 18 % counterpart in all measured indicators: density, reactivity, permeability, and NCC. These results confirm that, under optimized distribution conditions, 16 % pitch can outperform higher pitch levels due to better utilization and structural balance.

This finding emphasizes the importance of process design over formulation alone and validates the use of dual-pitch strategies for high-value applications.

4.3 Energy–Structure Trade-off

The use of HSP, while advantageous for structural cohesion and reduced reactivity, comes at the cost of a lower internal energy contribution during baking. As the distillation of HSP removes light volatiles, the total degassing and in-situ combustion during firing are reduced. This effect was quantified by comparing baking losses and calculating an energy shortfall of 0.33 GJ/t for M3 (16 %), corresponding to approximately 9 Nm³/t of additional natural gas.

This introduces a trade-off between structural optimization and energy efficiency. However, the structural and environmental gains, especially reduced PAH emissions, improved dimensional stability, and lower carbon consumption are likely to outweigh the added energy input, particularly in facilities with environmental constraints or advanced heat recovery systems.

The observation also underlines the need to adjust baking curves when high-softening-point pitches are introduced, to avoid thermal imbalance and defect formation.

4.4 Process Implications and Industrial Transfer

The findings of this study have direct implications for the industrialization of sequenced mixing protocols. First, the feasibility of operating with two distinct pitch qualities, at two temperature levels, requires process adaptations:

- Mixing equipment must allow for precise thermal control and sequential addition, ideally with multi-stage mixing capabilities and reinforced materials to handle 240 °C pitch.
- Pitch logistics must support the preparation, storage, and handling of both LSP and HSP fractions, with controlled viscosity specifications.
- Baking operations must compensate for reduced energy input by adjusting combustion profiles or gas injection rates.

From a product perspective, the optimized M3 protocol enables enhanced anode quality without increasing pitch consumption, which may reduce overall emissions and operating costs. It provides a path forward for next-generation anode formulations, particularly under increasing environmental and energy efficiency demands.

The method also opens new avenues for recycling, integration and pitch refinement, including tuning distillation and fluxing parameters to customize pitch behaviour for sequenced applications.

Sequenced mixing, especially using tailored pitch rheologies, presents a scalable innovation with measurable performance gains. However, successful industrial implementation depends on:

- High-temperature-capable mixers (> 240 °C)
- Fine control of preheating protocols
- Adapted baking cycles

The energy contribution of pitch during baking is not only a function of its total volatile content, but also of the molecular weight distribution of these volatiles. Light compounds, such as naphthalene or anthracene, volatilize at relatively low temperatures (200–350 °C) and combust early in the baking cycle, providing a sharp but transient energy release. Heavier aromatic compounds, including fluoranthene or chrysene, require higher temperatures (400–550 °C) to volatilize and burn more gradually, contributing to a more sustained internal heating of the anode. This molecular profile affects both the thermal profile and the structural evolution of the green anode during baking. As such, tailoring pitch composition by controlling softening point and distillation cuts can directly influence the efficiency and safety of the firing process. These observations align with recent studies on pitch pyrolysis behaviour and carbonization modelling [12, 13].

The reduction of PAHs, increased coking value, and lower NCC all support the environmental and economic justification for deployment. A transition to this method may be particularly suited for revamping existing facilities.

5. Conclusion

This work demonstrates that sequenced pitch mixing, when executed with rheologically tailored coal tar pitches, significantly improves carbon anode performance compared to conventional one-step mixing. By decoupling the roles of impregnation and surface coating, the dual-stage M3 protocol achieves superior pitch distribution, reduced air permeability, lower reactivity, and a measurable reduction in net carbon consumption (NCC). At 16 % pitch content, M3 anodes consistently outperformed M1 references, confirming the value of thermal and structural control during mixing.

Furthermore, the study underlines the limits of pitch overdosage: increasing pitch content to 18 % consistently led to higher porosity, reactivity, and carbon consumption across all protocols. These results confirm that performance gains hinge not only on pitch quantity but also critically on how and when the pitch is introduced.

The mixing sequence strategy described here is readily compatible with industrial platforms such as the Intensive Mixing Cascade (IMC), offering a scalable path toward more efficient and environmentally robust anode production. Beyond immediate structural and electrical benefits, the approach also has implications for the baking process, where altered volatile profiles must be accounted for in energy balance and furnace operation.

Looking ahead, the use of biosourced fluxing agents, as described in many studies such as modified vegetal pitches or light fractions derived from renewable feedstocks could offer an additional lever for process optimization [14, 15]. These materials, when blended with conventional coal tar pitches, may reduce environmental impact while maintaining or enhancing binder performance. Their application as low-viscosity agents in the first mixing stage appears particularly promising, and merits future investigation in combination with sequenced mixing protocols.

Altogether, this work supports a paradigm shift from single-step pitch dosing to a more controlled, staged approach, unlocking new performance and sustainability avenues in anode manufacturing.

6. Acknowledgements

The authors gratefully acknowledge the support of Aluminium Dunkerque for providing the raw materials used in this study. The preparation of dry aggregates, including crushing and screening, was carried out with the assistance of Fives FCB's pilot testing centre. The baking of the laboratory anodes and their complete physical characterization were performed by R&D Carbon Ltd, whose technical expertise in carbon anode evaluation was instrumental in interpreting the results. The authors also wish to thank the CNRS / Institut de Science des Matériaux de Mulhouse (IS2M) for their scientific collaboration, with special recognition to Prof. Roger Gadiou and Dr. Laurent Vonna for their insights into pitch-coke interactions and support throughout the project.

7. References

1. Christophe Bouché, Vincent Philippaux et al, Rhodax Process – Recent Evolution and Future Challenges, Proceedings of the 42nd ICSOBA Conference, 27 – 31 October 2024, Lyon, France, *TRAVAUX 53*, 839-853.
2. Rajesh Garg, Hesham Buhazza et al., Improving Prebaked Anodes Electrical Resistivity in Aluminium Bahrain (ALBA), Proceedings of the 41st ICSOBA Conference, 5 – 9 November 2023, Dubai, UAE, *TRAVAUX 52*, 1151-1161.
3. Magali Gendre, François Morales et al., From Technology Development to Successful Star-Up and Operations of Sohar: The Potential of the Bi-Eirich Mixing Line, *Light Metals 2010*, p.963-968
4. Quentin Bernabé, Salima Belbachir et al., How to Appreciate the Coal Tar Pitch Impregnation on Coke Material?, *Light Metals 2019*, p.1195-1203.
5. Belkacem Amara, Duygu Kocaefe and Yasar Kocaefe, Effect of Wood Type on Biocoke Wettability by Coal Tar Pitch, Proceedings of the 42nd ICSOBA Conference, 27 – 31 October 2024, Lyon, France, *TRAVAUX 53*, 999-1008.
6. Armita Rastegari, Improvement of Anode Quality Through Pitch Modification, PhD Thesis, *University of Quebec at Chicoutimi (UQAC)*, 2023

7. Salima Belbachir, Jean-François André et al., Process for Producing a Carbon Paste for the Manufacture of High-Density Electrodes, *International Patent*, WO2016107998A1, published July 7, 2016, Fives Solios.
8. Werner K Fischer, Felix Keller et al., Interdependence between anode net consumption and pot design, pot operating parameters and anode properties. *Light metals*, 1991, vol. 681.
9. Zakariyya Uba Zango, Nonni Soraya Sambudi et al., An Overview and Evaluation of Highly Porous Adsorbent Materials for Polycyclic Aromatic Hydrocarbons and Phenols Removal from Wastewater, *Water*, 2020, **12** (10), 2921.
10. O. Anatole von Lilienfeld, Denis Andrienko, Coarse-grained interaction potentials for polyaromatic hydrocarbons, *J Chem Phys*, 2006, 124, issue 5
11. J. Boehm, R. F. Klie, J. Sun and L. D. Marks, Effect of Polycyclic Aromatic Hydrocarbon Size on π - π Interaction Strength with Graphitic Carbon, *The Journal of Physical Chemistry C*, 2016, **120** (47), p. 27028–27036.
12. M. Soltani Hosseini, M. Ardebili, A. Ebrahimi, Modeling the Coal Tar Pitch Primary Carbonization Process, *Fuels*, 2022, **3**(4), p. 576–589.
13. W. Liu, Z. Zhou, C. Liu, Reaction Behavior of a Trace Element during the Pitch Pyrolysis Process, *ACS Omega*, 2020, **5**(30), p. 18633–18639.
14. Asem Hussein and Houshang Alamdari, Towards Utilization of Bio-binders in Carbon Anodes for Aluminum Industry, Proceedings of the 41st ICSOBA Conference, 5 – 9 November 2023, Dubai, UAE, *TRAVAUX 52*, 1025-1033.
15. Marie Aimee Tuyizere Flora, Guillaume Gauvin et al., Bio-pitch Improvement for Coal Tar Pitch Replacement in Pre-baked Anodes, Proceedings of the 41st ICSOBA Conference, 5 – 9 November 2023, Dubai, UAE, *TRAVAUX 52*, 1047-1059.

